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Revolutionizing Green Catalysis: A Novel Amla Seeds Derived Biochar Modified g-C_3N_4·SO_3H Catalyst for Sustainable and Versatile Synthesis of Bis-Indoles

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1. Experimental Section:

1.1. Material and methods:

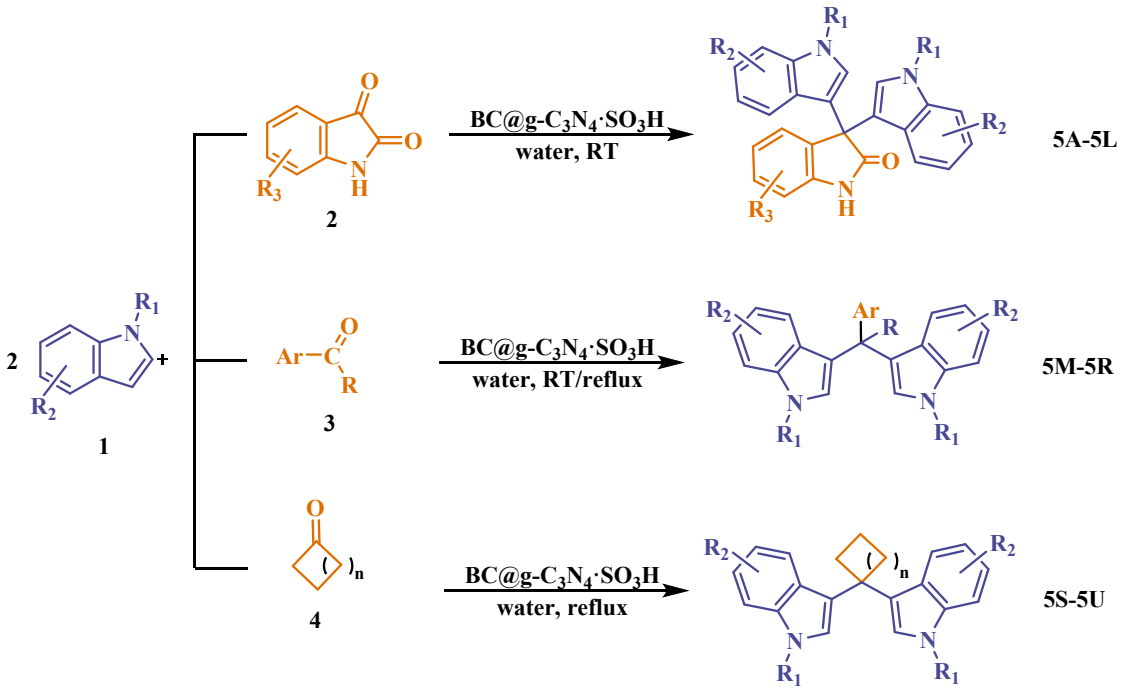
The chemicals used in this study were sourced from Sigma-Aldrich, Loba-Chemie, and Merck, ensuring high quality. They were utilized as received, without additional purification, underscoring their exceptional purity. Melting points were precisely measured using an electric thermal melting point apparatus. The reaction progress was monitored using thin-layer chromatography on advanced silica gel 60 RP-18 F254S plates, with visualization under UV lamps. The catalyst's IR spectrum was meticulously recorded with a Bruker FTIR spectrometer, providing detailed chemical composition analysis. X-ray diffraction (XRD) data were acquired with the Rigaku Ultima IV diffractometer, delivering precise information on crystalline properties. Comprehensive characterization included Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX), and Mapping using the F E I Quanta FEG 200 system, which offered detailed insights into the catalyst's morphology and structure. Thermal stability and composition were analyzed using TGA/DTA on the Hitachi NEXTA STA300 system. Additionally, ^{1}H and ^{13}C NMR spectra were recorded with high accuracy using the JEOL 400 MHz instrument, with $CDCl_3$ and DMSO-d_6 as solvents and TMS as the internal standard, ensuring reliable structural elucidation.

General procedure for the synthesis of Bis-indole derivatives:

In a 25 mL round-bottom flask, 4 mL of water was combined with 0.5 mmol of indole and 0.25 mmol of a second reactant containing carbonyl group such as isatins, aldehydes, acetophenone, cyclo-ketones, or dimedone along with 20 mg of BCNSA catalyst. The mixture was stirred at room temperature or under reflux for an appropriate duration, with the reaction progress monitored by TLC. During the reaction, the color of the mixture exhibited a notable transformation, shifting from lighter to darker shades, and in some cases, changing from white to dark red, pink, or orange upon completion. After the reaction, the mixture was dried under vacuum, and the catalyst was removed using methanol. The filtrate was dried, washed with lukewarm water to remove any residual impurities, and dried again. The melting point of the final product was determined, followed by analysis using melting point, ^{1}H and ^{13}C NMR spectroscopy to confirm its purity and verify successful synthesis.

2. Green Chemistry Metrics:

The green chemistry metrics for all synthesized compounds has been determined using the corresponding parameters of each compound[1, 2] **(Table S1).**



Environmental factor (E-factor)

E-factor = mass of waste/ mass of product

Where the mass of waste = total mass of raw materials minus the total mass of the product

Atom-economy (AE)

The ideal valve of the AE factor is 100% means all starting material is converted into the product.

AE = MW of product ÷ Σ (MW of stoichiometric reactants) × 100

Process mass intensity (PMI)

PMI = Σ (mass of stoichiometric reactants + solvent) / mass of product

Reaction mass efficiency (RME)

RME = mass of product /Σ (mass of stoichiometric reactants) × 100

(Higher value measures the **cleanness** of reaction)

Eco-score (E-score)

Ideal reactions Eco-score value is 100.

Eco-scale from 0 to 100 using the following scores: > 75, excellent; > 50, acceptable; and < 50, inadequate.

E-score has been calculated for the reaction based on the following 6 parameters below.

S. No.	*Parameter*
1	Yield
2	Price of the reaction component
3	Safety (Reactant)[a]
4	Technical setup
5	Temperature /time
6	Workup and purification
	Total penalty points
	Based on the hazard warning symbols

Eco-Score = 100 – the sum of individual penalties

(>75, excellent synthesis)

Table S1: Green chemistry matrix of synthesized bis-indole scaffolds.

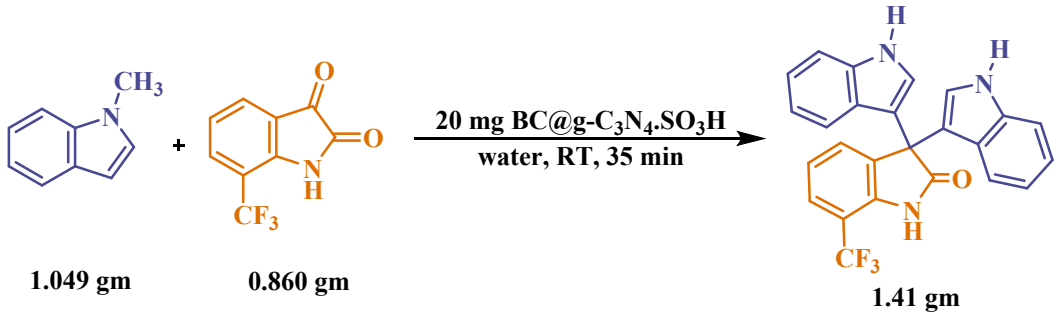
Code	Yield (%)	E factor	AE (%)	RME	PMI	Eco-Score
5A	85.47	0.216174	96.20341	82.22505	1.228915	72.735
5B	83.62	0.242039	96.28408	80.51275	1.254021	71.81
5C	96.26	0.082974	95.92595	92.33832	1.095022	78.13
5D	95.86	0.089335	95.7637	91.79909	1.102083	77.93
5E	**98.48**	**0.064164**	95.42086	**93.97046**	1.077486	**79.24**
5F	95.02	0.09524	96.08948	91.30422	1.106457	77.51
5G	98.11	0.066427	95.57749	93.77108	**1.079455**	79.055
5H	97.65	0.075644	95.20489	92.96757	1.089744	78.825
5I	96.85	0.07766	95.8117	92.79363	1.089365	78.425
5J	88.53	0.177983	95.88939	84.89087	1.19056	74.265
5K	81.57	0.280688	95.72517	78.08302	1.294908	70.785
5L	89.77	0.158256	96.17543	86.33668	1.169199	74.885
5M	94.03	0.115527	95.33522	89.6437	1.129855	77.015

5N	83.12	0.249228	**96.30585**	80.04942	1.261913	71.56
5O	91.06	0.144867	95.92177	87.34636	1.157751	75.53
5P	96.13	0.087711	95.63735	91.93619	1.100676	78.065
5Q	87.78	0.1879	95.90134	84.1822	1.201327	73.89
5R	84.97	0.233239	95.43046	81.08726	1.248798	72.485
5S	95.43	0.105585	**94.78138**	90.44987	1.121549	77.715
5T	93.51	0.125873	94.98446	88.81997	1.141498	76.755
5U	**80.01**	**0.308722**	95.50109	**76.41043**	**1.324987**	**70.005**

This method demonstrates outstanding green metrics, including a low E-factor (0.064–0.30), high atom economy (94.78–96.30%), excellent reaction mass efficiency (76.41–93.97%), and superior process mass intensity (1.07–1.32). Furthermore, the eco-score (70–79.24) highlights its minimal environmental footprint. These findings underscore the potential of BCNSA catalysts in advancing sustainable, eco-friendly synthesis, offering an efficient approach with minimal environmental impact.

3. Gram scale synthesis:

We tested this methodology for its potential industrial application by performing a gram-scale synthesis using 1-methylindole and 7-(trifluoromethyl)isatin at room temperature with 20 mg of catalyst, using water as the sole solvent. The reaction was completed in just 35 minutes, as monitored by TLC. Notably, upon completion of the reaction, the mixture underwent a distinct color change to hot pink. This color shift is characteristic of the process, though the specific hue may vary depending on the reactants involved. After the reaction, the mixture was filtered to remove the catalyst, which was then washed away with acetone. The filtrate was dried, rinsed with lukewarm water, and dried again. The yield was calculated to be 81.97% (1.72 g).



1.049 gm **0.860 gm** **1.41 gm**

4. NMR and Mass spectra of synthesized bis-indole derivatives:

5A: 1,1''-dimethyl-7'-(trifluoromethyl)-1*H*,1''*H*-[3,3':3',3''-terindol]-2'(1'*H*)-one

Saffron coloured powder, M.P.: 230-234 ^{o}C,^{1}H NMR (400 MHz, DMSO-d_6) δ 11.11 (s, 1H, NH), 7.51 (d, *J* = 7.9 Hz, 1H, ArH), 7.46 (d, *J* = 7.3 Hz, 1H, ArH), 7.37 (s, 1H, ArH), 7.35 (s, 1H, ArH), 7.18 (s, 1H, ArH), 7.16 (s, 1H, ArH), 7.10 – 7.04 (m, 3H, ArH), 6.86 (s, 2H, ArH), 6.84 – 6.80 (m, 2H, ArH), 3.68 (s, 6H, N-CH_3).^{13}C NMR (101 MHz, DMSO-d_6) δ 179.42, 137.92, 136.65, 129.42, 129.14, 126.28, 122.41, 121.78, 121.15, 119.19, 115.46, 112.91, 110.51, 51.99, 32.91. ESI–MS (m/z): 459.1558 [M^+] for $C_{27}H_{20}F_3N_3O$.

5B: 6,6''-dichloro-7'-(trifluoromethyl)-1*H*,1''*H*-[3,3':3',3''-terindol]-2'(1'*H*)-one

Brown solid, M.P.: 182-186 ^{o}C,^{1}H NMR (400 MHz, DMSO-d_6) δ 11.19 (d, *J* = 2.2 Hz, 2H, NH), 11.15 (s, 1H, NH), 7.52 (d, *J* = 8.0 Hz, 1H, ArH), 7.45 (d, *J* = 7.4 Hz, 1H, ArH), 7.38 (d, *J* = 1.8 Hz, 2H, ArH), 7.11 (d, *J* = 8.7 Hz, 3H, ArH), 6.86 (d, *J* = 2.5 Hz, 2H, ArH), 6.83 (d, *J* = 1.9 Hz, 1H, ArH), 6.81 (d, *J* = 1.9 Hz, 1H, ArH). ^{13}C NMR (101 MHz, DMSO-d_6) δ 179.25, 137.88, 136.15, 127.82, 126.53, 126.02, 124.71, 122.52, 122.16, 119.51, 114.04, 112.70, 111.92, 111.21, 109.99, 109.78, 51.82. ESI–MS (m/z): 499.0466 [M^+], Found: 499.0357 for $C_{25}H_{14}Cl_2F_3N_3O$.

5C: 7'-(trifluoromethyl)-1*H*,1''*H*-[3,3':3',3''-terindol]-2'(1'*H*)-one

Beige coloured powder, M.P.: 242-246 ^{o}C[3],^{1}H NMR (400 MHz, DMSO-d_6) δ 11.09 (s, 1H, NH), 11.03 (d, *J* = 2.1 Hz, 2H, NH), 7.50 (d, *J* = 8.0 Hz, 1H, ArH), 7.45 (d, *J* = 7.4 Hz, 1H, ArH), 7.33 (d, *J* = 8.2 Hz, 2H, ArH), 7.17 (d, *J* = 8.1 Hz, 2H, ArH), 7.08 (t, *J* = 7.7 Hz, 1H, ArH), 7.01 – 6.97 (m, 2H, ArH), 6.82 (d, *J* = 2.5 Hz, 2H, ArH), 6.81 – 6.76 (m, 2H, ArH). ^{13}C NMR (101 MHz, DMSO-d_6) δ 179.61, 139.13, 137.47, 136.76, 129.44, 125.95, 124.97, 122.96, 122.27 , 121.65, 120.98, 119.00, 113.84, 112.30, 111.01, 52.18. ESI–MS (m/z): 431.1245 [M^+] for $C_{25}H_{16}F_3N_3O$.

5D: 5'-fluoro-1,1''-dimethyl-1*H*,1''*H*-[3,3':3',3''-terindol]-2'(1'*H*)-one

Beige powder, M.P.: 262-266 ^{o}C[4],^{1}H NMR (400 MHz, DMSO-d_6) δ 10.65 (s, 1H, NH), 7.36 (s, 1H, ArH), 7.34 (s, 1H, ArH), 7.20 (s, 1H, ArH), 7.18 (s, 1H, ArH), 7.07 – 7.03 (m, 3H, ArH), 7.02 – 6.98 (m, 1H, ArH), 6.94 (dd, *J* = 8.4, 4.5 Hz, 1H, ArH), 6.90 (s, 2H, ArH), 6.81 (ddd, *J* = 8.0, 7.1, 0.9 Hz, 2H, ArH), 3.68 (s, 6H, N-CH_3). ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.98, 157.19, 153.46, 137.99, 137.97, 137.82, 136.63, 129.10, 126.36, 121.69, 121.28, 119.09, 113.22, 110.40, 53.40, 32.89. ESI–MS (m/z): 409.1590 [M^+] for $C_{26}H_{20}FN_3O$.

5E: 5'-fluoro-1*H*,1''*H*-[3,3':3',3''-terindol]-2'(1'*H*)-one

Creamy white solid, M.P.: 258-262 ^{o}C[4],[1]H NMR (400 MHz, DMSO-d_6) δ 10.99 (d, *J* = 2.3 Hz, 2H, NH), 10.63 (s, 2H, NH), 7.33 (d, *J* = 0.8 Hz, 1H, ArH), 7.31 (d, *J* = 0.8 Hz, 1H, ArH), 7.18 (s, 1H, ArH), 7.16 (s, 1H, ArH), 7.06 – 7.01 (m, 1H, ArH), 7.00 – 6.98 (m, 3H, ArH), 6.97 – 6.92 (m, 1H, ArH), 6.85 (d, *J* = 2.6 Hz, 2H, ArH), 6.78 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 2H, ArH). ^{13}C NMR (101 MHz, DMSO-d_6) δ 179.18, 159.62, 157.26, 138.04, 137.43, 136.82, 126.04, 126.03, 126.02, 124.95, 121.56, 121.11, 118.89, 114.12, 112.22, 53.59. ESI–MS (m/z): 381.1277 [M^+] for $C_{24}H_{16}FN_3O$.

5F: 5'-bromo-1,1''-dimethyl-1*H*,1''*H*-[3,3':3',3''-terindol]-2'(1'*H*)-one

Pale white crystalline soild, M.P.: 284-292 ^{o}C[4],[1]H NMR (400 MHz, DMSO-d_6) δ 10.77 (s, 1H, NH), 7.40 – 7.37 (m, 2H, ArH), 7.35 (s, 1H, ArH), 7.26 (d, *J* = 2.0 Hz, 1H, ArH), 7.18 (s, 1H, ArH), 7.16 (s, 1H, ArH), 7.08 – 7.04 (m, 2H, ArH), 6.92 (d, *J* = 8.3 Hz, 1H, ArH), 6.89 (s, 2H, ArH), 6.84 – 6.80 (m, 2H, ArH), 3.68 (s, 6H, N-CH_3). ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.59, 141.10, 137.84, 137.35, 131.32, 129.04, 127.84, 126.32, 121.74, 121.19, 119.14, 113.80, 113.09, 112.26, 110.47, 53.11, 32.90. ESI–MS (m/z): 469.0790 [M^+] for $C_{26}H_{20}BrN_3O$.

5G: 1,1''-dimethyl-1*H*,1''*H*-[3,3':3',3''-terindol]-2'(1'*H*)-one

Snow white powder, M.P.: 282-286 ^{o}C[4],[1]H NMR (400 MHz, DMSO-d_6) δ 10.61 (s, 1H, NH), 7.35 (s, 1H, ArH), 7.33 (s, 1H, ArH), 7.19 (dd, *J* = 7.7, 4.8 Hz, 4H, ArH), 7.06 – 7.02 (m, 2H, ArH), 6.94 (dd, *J* = 8.2, 0.9 Hz, 1H, ArH), 6.89 (td, *J* = 7.6, 1.0 Hz, 1H, ArH), 6.84 (s, 2H, ArH), 6.80 (ddd, *J* = 8.0, 7.1, 0.9 Hz, 1H, ArH), 3.66 (s, 6H, N-CH_3). ^{13}C NMR (101 MHz, DMSO-d_6) δ 179.08, 141.75, 137.81, 135.00, 128.97, 128.45, 126.51, 125.40, 122.12, 121.52, 118.94, 113.90, 113.88, 110.31, 110.14, 52.88, 32.87. ESI–MS (m/z): 391.1685 [M^+] for $C_{26}H_{21}N_3O$.

5H: 1*H*,1''*H*-[3,3':3',3''-terindol]-2'(1'*H*)-one

Dull white powder, M.P.: 264-270 ^{o}C[4],[1]H NMR (400 MHz, DMSO-d_6) δ 10.95 (s, 2H, NH), 10.60 (s, 1H, NH), 7.32 (d, *J* = 8.1 Hz, 2H, ArH), 7.20 (d, *J* = 7.7 Hz, 4H, ArH), 6.97 (dd, *J* = 14.0, 7.3 Hz, 3H, ArH), 6.88 (t, *J* = 7.5 Hz, 1H, ArH), 6.82 (d, *J* = 2.4 Hz, 2H, ArH), 6.76 (t, *J* = 7.5 Hz, 2H, ArH). ^{13}C NMR (101 MHz, DMSO-d_6) δ 179.30, 141.84, 137.44, 135.12, 128.38, 126.21, 125.44, 124.81, 122.00, 121.39, 118.76, 114.79, 112.14, 110.10, 53.08. ESI–MS (m/z): 363.1372 [M^+] for $C_{24}H_{17}N_3O$.

5I: 5'-bromo-1*H*,1''*H*-[3,3':3',3''-terindol]-2'(1'*H*)-one

Light pink solid, M.P.: 238-242 ^{o}C[4], ^{1}HNMR (400 MHz, DMSO-d_6) δ 11.01 (d, J = 2.0 Hz, 2H, NH), 10.76 (s, 1H, NH), 7.39 (dd, J = 8.3, 2.0 Hz, 1H, ArH), 7.33 (d, J = 8.2 Hz, 2H, ArH), 7.26 (d, J = 1.9 Hz, 1H, ArH), 7.16 (d, J = 8.1 Hz, 2H, ArH), 7.00 (dd, J = 11.2, 3.9 Hz, 2H, ArH), 6.93 (d, J = 8.3 Hz, 1H, ArH), 6.85 (d, J = 2.5 Hz, 2H, ArH), 6.79 (t, J = 7.5 Hz, 2H, ArH). ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.78, 141.19, 137.47, 131.23, 127.87, 125.99, 124.96, 121.61, 121.02, 118.96, 113.98, 113.67, 112.25, 53.30. ESI–MS (m/z): 441.0477 [M^+] for $C_{24}H_{16}BrN_3O$.

5J: 6,6''-dichloro-5'-fluoro-1*H*,1''*H*-[3,3':3',3''-terindol]-2'(1'*H*)-one

Cream coloured solid, M.P.: 278-282 ^{o}C,^{1}H NMR (400 MHz, DMSO-d_6) δ 11.15 (d, *J* = 1.7 Hz, 2H, NH), 10.70 (s, 1H, NH), 7.38 (d, *J* = 1.7 Hz, 2H, ArH), 7.14 (d, *J* = 8.6 Hz, 2H, ArH), 7.08 – 7.00 (m, 2H, ArH), 6.96 – 6.91 (m, 3H, ArH), 6.82 (dd, *J* = 8.6, 1.8 Hz, 2H, ArH). ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.81, 159.62, 157.26, 137.98, 137.96, 137.86, 136.19, 136.11, 126.45, 125.98, 124.79, 122.32, 119.40, 114.35, 111.83, 53.23. ESI–MS (m/z): 449.0498 [M^+] for $C_{24}H_{14}Cl_2FN_3O$.

5K: 6,6''-dichloro-1*H*,1''*H*-[3,3':3',3''-terindol]-2'(1'*H*)-one

Orange solid, M.P.: 290-294 ^{o}C[5],^{1}H NMR (400 MHz, DMSO-d_6) δ 11.11 (d, *J* = 2.7 Hz, 2H, NH), 10.66 (s, 1H, NH), 7.37 (d, *J* = 2.3 Hz, 3H, ArH), 7.22 – 7.13 (m, 3H, ArH), 6.96 – 6.86 (m, 3H, ArH), 6.80 (dd, *J* = 8.7, 2.1 Hz, 3H, ArH). ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.90, 141.73, 137.84, 134.49, 128.63, 126.36, 125.80, 125.33, 124.94, 122.45, 122.21, 119.26, 114.99, 111.77, 110.32, 52.71. ESI–MS (m/z): 431.0592 [M^+] for $C_{24}H_{15}Cl_2N_3O$.

5L: 5'-bromo-6,6''-dichloro-1*H*,1''*H*-[3,3':3',3''-terindol]-2'(1'*H*)-one

White solid, M.P.: 268-272 ^{o}C,^{1}H NMR (400 MHz, DMSO-d_6) δ 11.16 (d, *J* = 2.1 Hz, 2H, NH), 10.82 (s, 1H, NH), 7.41 – 7.35 (m, 3H, ArH), 7.26 (d, *J* = 1.9 Hz, 1H, ArH), 7.13 (s, 1H, ArH), 7.11 (s, 1H, ArH), 6.91 (dd, *J* = 13.1, 5.4 Hz, 3H, ArH), 6.82 (dd, *J* = 8.6, 1.9 Hz, 2H, ArH). ^{13}C NMR (101 MHz, DMSO-d_6) δ 178.42, 141.09, 137.86, 136.83, 131.51, 127.80, 125.99, 124.73, 122.22, 119.46, 114.19, 114.18, 114.17, 113.89, 112.44, 111.90, 52.92. ESI–MS (m/z): 508.9697 [M^+] for $C_{24}H_{14}BrCl_2N_3O$.

5M: 5-(bis(1-methyl-1*H*-indol-3-yl)methyl)-4-methylthiazole

Peach coloured solid, M.P.: 238-242 ^{o}C,^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (s, 1H, ArH), 7.42 (d, *J* = 7.9 Hz, 2H, ArH), 7.33 (d, *J* = 8.2 Hz, 2H, ArH), 7.25 (t, *J* = 7.5 Hz, 2H, ArH), 7.06 (t,

J = 7.4 Hz, 2H, ArH), 6.63 (s, 2H, ArH), 6.11 (s, 1H, CH), 3.70 (s, 6H, N-CH_3), 2.50 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.87, 148.03, 137.42, 127.81, 127.01, 121.84 , 119.78, 119.06, 117.34, 109.43, 32.92, 32.10, 15.44. ESI–MS (m/z): 371.1456 [M^+], Found: 371.1428 for $C_{23}H_{21}N_3S$.

5N: 3,3'-(pyren-1-ylmethylene)bis(1-methyl-1*H*-indole)

Vine coloured solid, M.P.: 182-186 ^oC,^{1}H NMR (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 9.4 Hz, 1H, ArH), 8.18 – 8.14 (m, 2H, ArH), 8.04 – 7.97 (m, 5H, ArH), 7.87 (d, *J* = 8.0 Hz, 1H, ArH), 7.39 (d, *J* = 7.9 Hz, 2H, ArH), 7.31 (d, *J* = 8.2 Hz, 2H, ArH), 7.23 (dd, *J* = 8.1, 0.9 Hz, 2H, ArH), 7.01 – 6.99 (m, 2H, ArH, 1H, CH), 6.44 (s, 2H, ArH), 3.63 (s, 6H, N-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.29, 137.57, 131.49, 131.00, 130.01, 129.25, 128.75, 127.60, 126.80, 125.89, 125.24, 125.13, 125.02, 124.93 124.91, 123.93, 121.58, 120.14, 118.80, 118.24, 109.24, 36.18, 32.82. ESI–MS (m/z): 474.2096 [M^+], Found: 474.1881 for $C_{35}H_{26}N_2$.

5O: 4-(bis(1-methyl-1*H*-indol-3-yl)methyl)-2,6-dimethoxyphenol

Light pink powder, M.P.: 166-170 ^oC[6],^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.9 Hz, 2H, ArH), 7.30 (d, *J* = 8.2 Hz, 2H, ArH), 7.20 (t, *J* = 7.5 Hz, 2H, ArH), 7.00 (t, *J* = 7.4 Hz, 2H, ArH), 6.59 (s, 2H, ArH), 6.53 (s, 2H, ArH), 5.80 (s, 1H, OH), 5.43 (s, 1H, CH), 3.76 (s, 6H, OCH_3), 3.69 (s, 6H, N-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.88, 137.48, 135.84, 132.87, 128.35, 127.50, 121.50, 120.16, 118.71, 118.36, 109.16, 105.46, 56.36, 40.38, 32.83. ESI–MS (m/z): 426.1943 [M^+] for $C_{27}H_{26}N_2O_3$.

5P: 4-(bis(6-fluoro-1*H*-indol-3-yl)methyl)-N,N-dimethylaniline

Vine colour powdered solid, M.P.: 152-156 ^oC,^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (s, 2H, NH), 7.28 (s, 1H, ArH), 7.25 (s, 1H, ArH), 7.16 (d, *J* = 7.3 Hz, 2H, ArH), 7.00 (d, *J* = 9.6 Hz, 2H, ArH), 6.74 – 6.68 (m, 4H, ArH), 6.60 (s, 2H, ArH), 5.70 (s, 1H, CH), 2.91 (s, 6H, N-CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.11, 158.75, 136.62, 129.26, 123.77, 123.74, 120.75, 120.31, 112.89, 108.10, 107.85, 97.50, 97.25, 41.00, 39.21. ESI–MS (m/z): 401.1704 [M^+] for $C_{25}H_{21}F_2N_3$.

5Q: 3,3'-(1-(3,4-dimethoxyphenyl)ethane-1,1-diyl)bis(1-methyl-1*H*-indole)

Creamy yellow solid, M.P.: 134-138 ^oC, ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dd, *J* = 8.0, 0.8 Hz, 2H, ArH), 7.29 (d, *J* = 8.2 Hz, 2H, ArH), 7.17 (ddd, *J* = 8.2, 7.0, 1.0 Hz, 2H, ArH), 7.01 (d, *J* = 2.2 Hz, 1H, ArH), 6.96 – 6.89 (m, 3H, ArH), 6.75 (d, *J* = 8.5 Hz, 1H, ArH), 6.49 (s, 2H,

ArH), 3.86 (s, 3H, OCH_3), 3.67 (d, *J* = 2.6 Hz, 3H, OCH_3; 6H, N-CH_3), 2.34 (s, 3H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.12, 146.95, 141.30, 137.85, 128.15, 126.88, 123.56, 122.32, 121.12, 120.41, 118.44, 111.98, 110.36, 109.24, 55.85, 43.46, 32.75, 29.39. ESI–MS (m/z): 424.2151 [M^+], Found: 424.2140 for $C_{28}H_{28}N_2O_2$.

5R: 3,3'-(1-(p-tolyl)ethane-1,1-diyl)bis(1-methyl-1*H*-indole)

Beige coloured powder, M.P.: 170-174 °C[7], ^1H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.0 Hz, 2H, ArH), 7.29 (dd, *J* = 8.3, 2.2 Hz, 4H, ArH), 7.17 (ddd, *J* = 8.2, 7.0, 1.0 Hz, 2H, ArH), 7.06 (d, *J* = 8.0 Hz, 2H, ArH), 6.94 (ddd, *J* = 8.0, 7.0, 1.0 Hz, 2H, ArH), 6.50 (s, 2H, ArH), 3.67 (s, 6H, N-CH_3), 2.34 (d, *J* = 5.7 Hz, 6H, CH_3). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.46, 137.85, 135.10, 128.57, 127.09, 126.94, 123.55, 122.33, 121.07, 118.39, 109.22, 43.41, 32.73, 29.28, 21.11. ESI–MS (m/z): 378.2096 [M^+] for $C_{27}H_{26}N_2$.

5S: 3,3'-(cyclopentane-1,1-diyl)bis(1-methyl-1*H*-indole)

Dark pink powder, M.P.: 114-118 °C,^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.0 Hz, 2H, ArH), 7.25 (s, 1H, ArH), 7.23 (s, 1H, ArH), 7.15 – 7.11 (m, 2H, ArH), 6.95 – 6.91 (m, 4H, ArH), 3.73 (s, 6H, N-CH_3), 2.52 (s, 4H, CH_2), 1.84 (s, 4H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.93, 126.95, 126.14, 122.11, 121.43, 120.97, 118.06, 109.16, 46.18, 39.05, 32.79, 24.18. ESI–MS (m/z): 328.1939 [M^+], Found: 327.5009 for $C_{23}H_{24}N_2$.

5T: 3,3'-(cyclohexane-1,1-diyl)bis(1-methyl-1*H*-indole)

Moss coloured solid, M.P.: 166-170 °C[8],^1H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.4 Hz, 3H, ArH), 7.26 (d, *J* = 11.3 Hz, 2H, ArH), 7.14 (t, *J* = 8.3 Hz, 1H, ArH), 6.97 – 6.92 (m, 4H, ArH), 3.74 (s, 6H, N-CH_3), 2.59 – 2.56 (m, 4H, CH_2), 1.72 – 1.59 (m, 6H, CH_2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.78, 127.15, 126.80, 122.33, 121.76, 120.83, 118.04, 109.23, 39.77, 37.20, 32.83, 26.91, 23.17. ESI–MS (m/z): 342.2096 [M^+] for $C_{24}H_{26}N_2$.

5U:3,3-dimethyl-5,5-bis(1-methyl-1*H*-indol-3-yl)cyclohexan-1-one

Dark purple powdered solid, M.P.: 98-102 °C,^{1}HNMR (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 7.4 Hz, 2H, ArH), 7.34 (dd, *J* = 25.0, 18.5 Hz, 6H, ArH), 6.67 (s, 2H, ArH), 3.81 (s, 6H, N-CH_3), 2.66 (s, 3H, CH_2), 2.34 (s, 3H, CH_2), 1.13 (s, 6H, CH_3).^{13}C NMR (101 MHz, $CDCl_3$) δ 200.09, 153.05, 138.21, 130.83, 125.59, 123.04, 121.50, 120.36, 115.05, 110.12, 51.04, 42.72, 33.48, 33.40, 33.25, 28.64. ESI–MS (m/z): 384.2202 [M^+], Found: 385.2278 for $C_{26}H_{28}N_2O$.

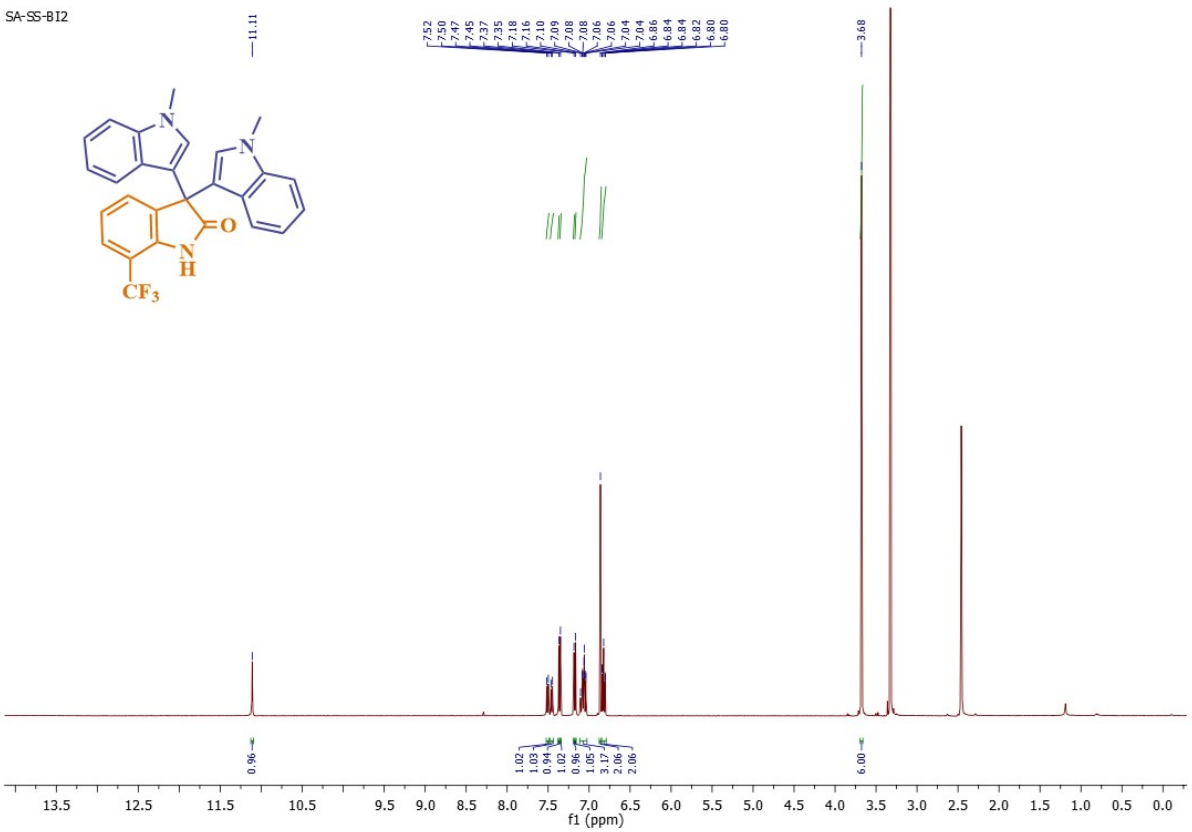


Figure S1: ^{1}H NMR spectrum of compound 5A.

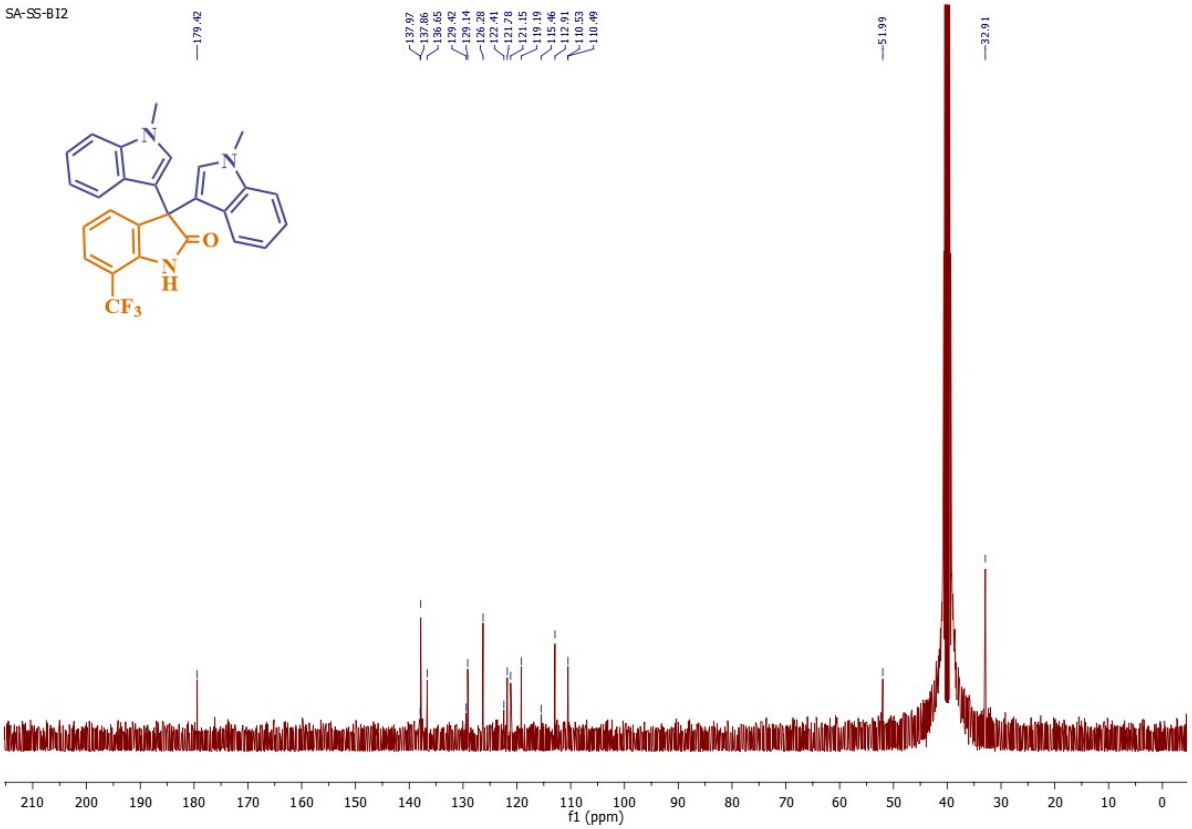


Figure S2: ^{13}C NMR spectrum of compound 5A.

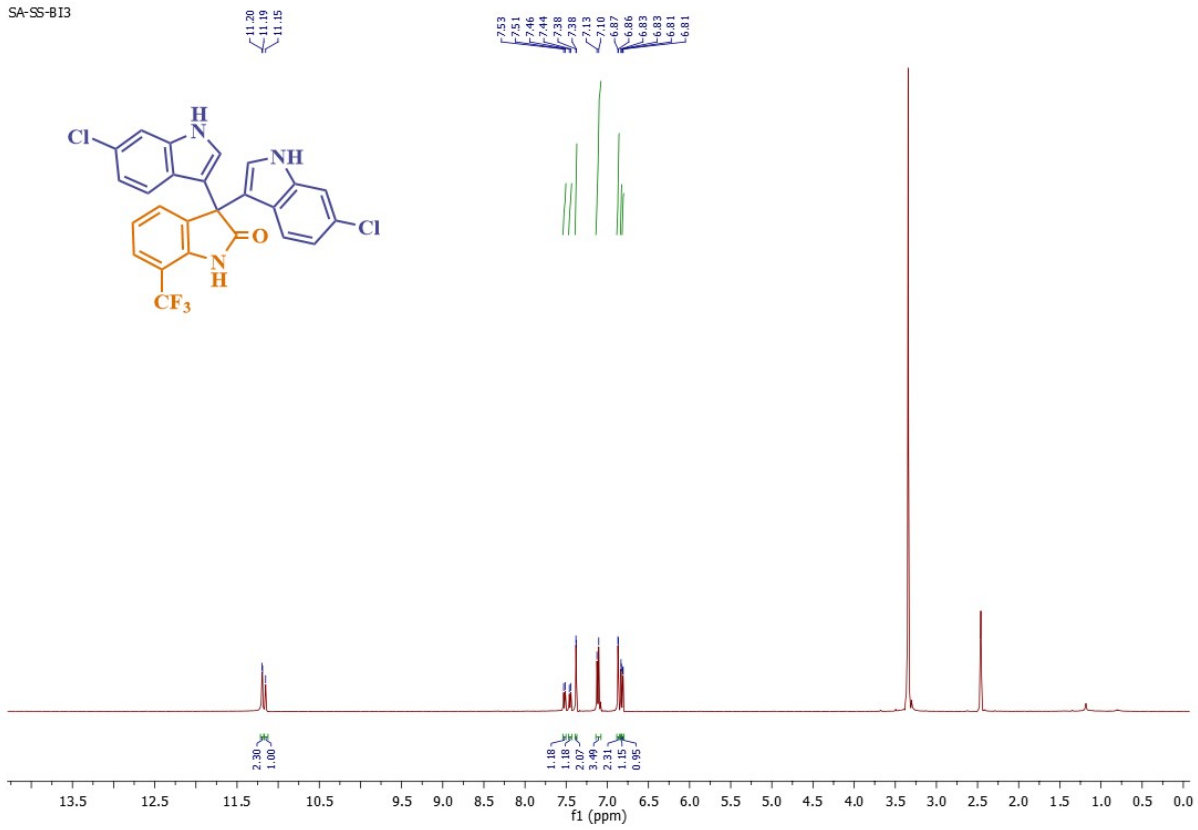


Figure S3:[1]H NMR spectrum of compound 5B.

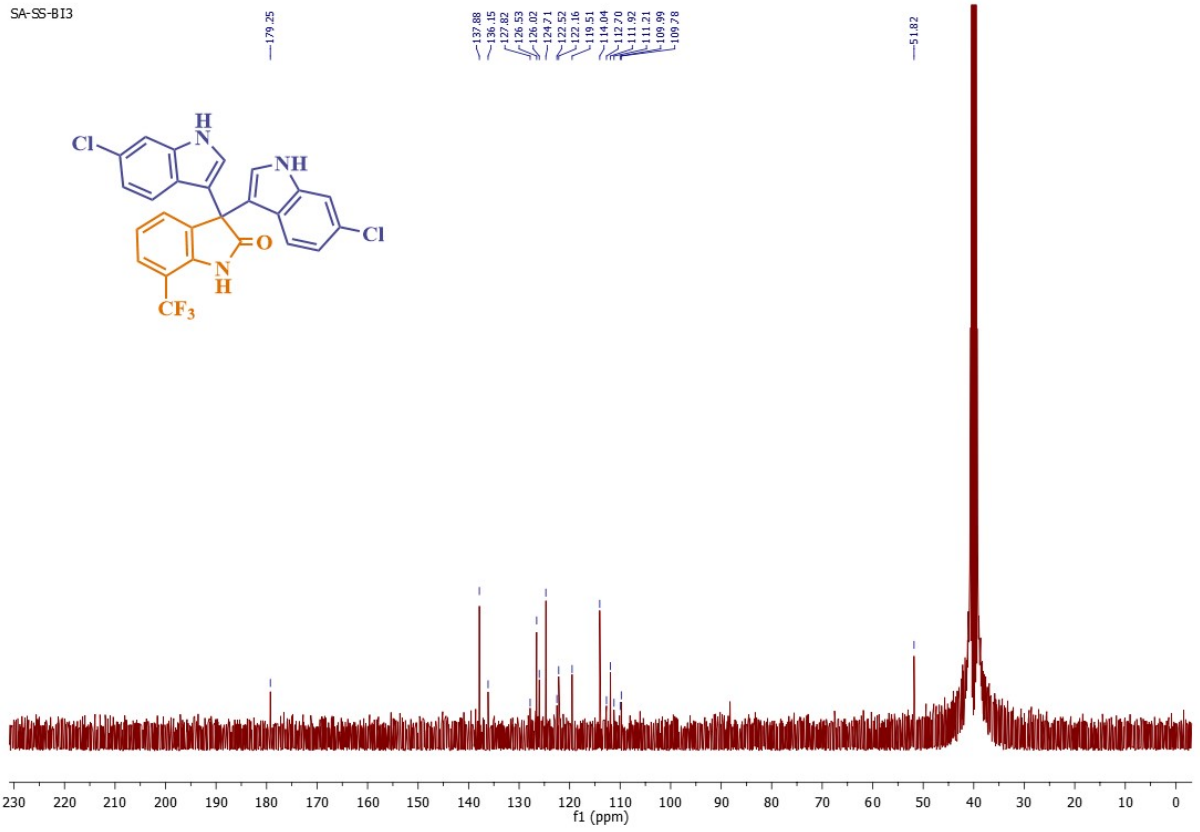


Figure S4:[13]C NMR spectrum of compound 5B.

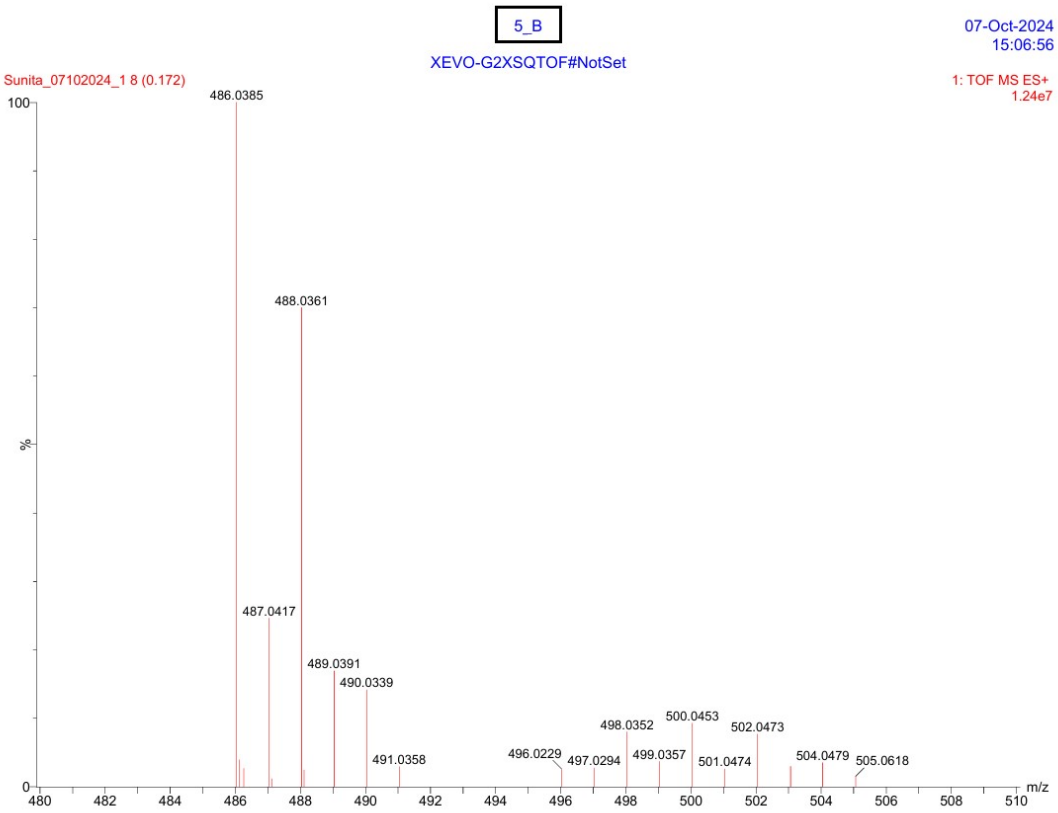


Figure S5: The HRMS profile of compound 5B.

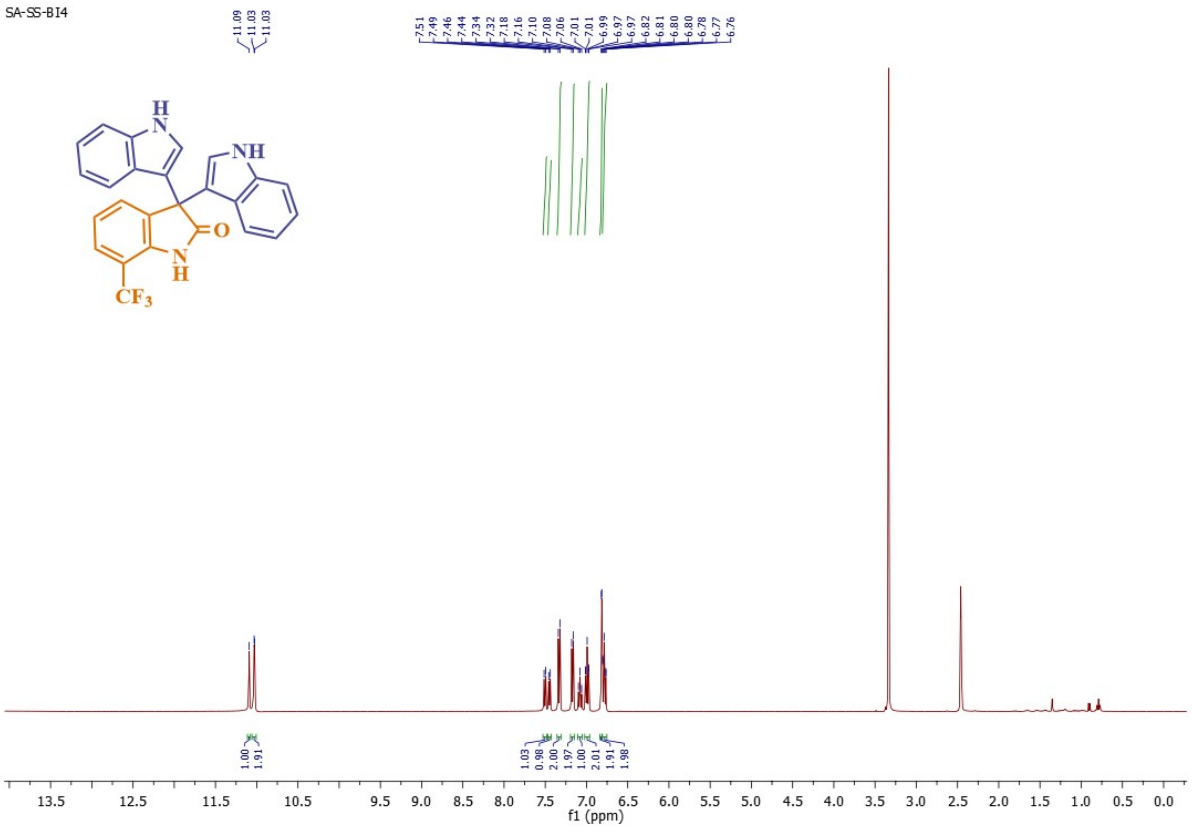


Figure S6: ^{1}H NMR spectrum of compound 5C.

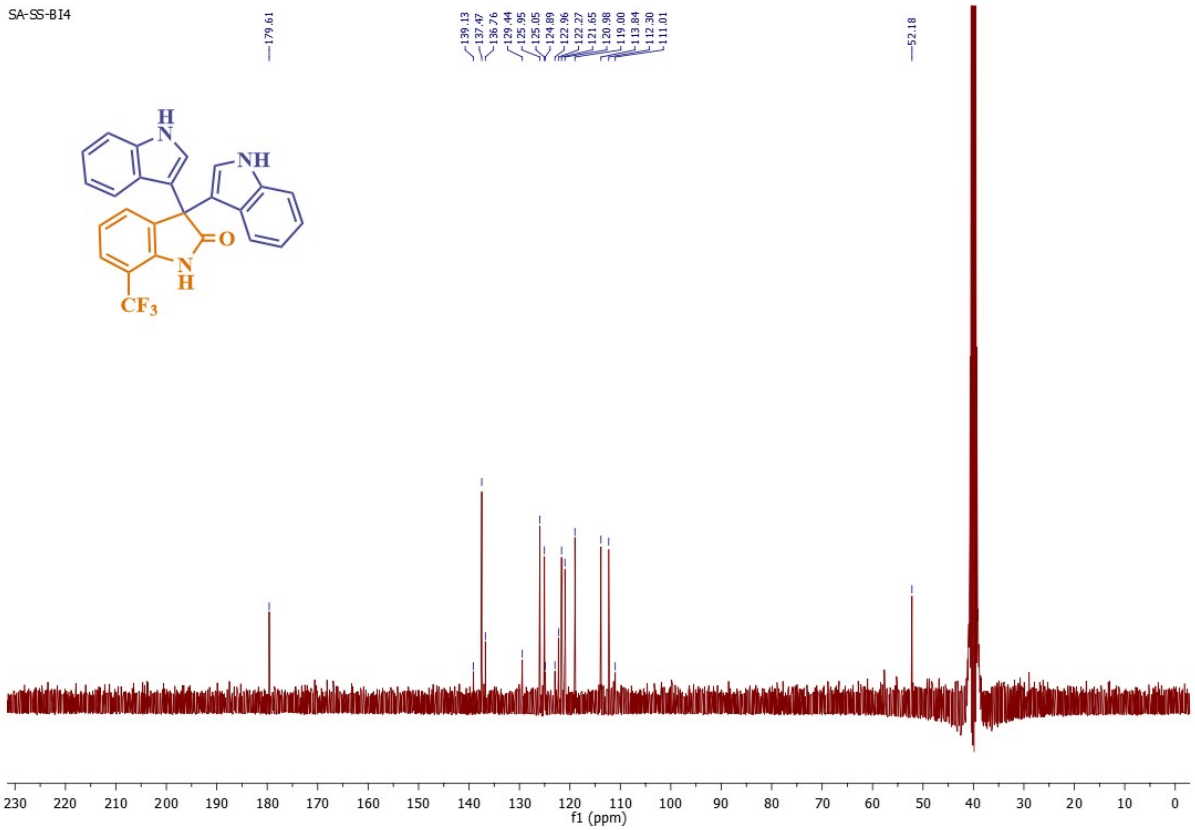


Figure S7: ^{13}C NMR spectrum of compound 5C.

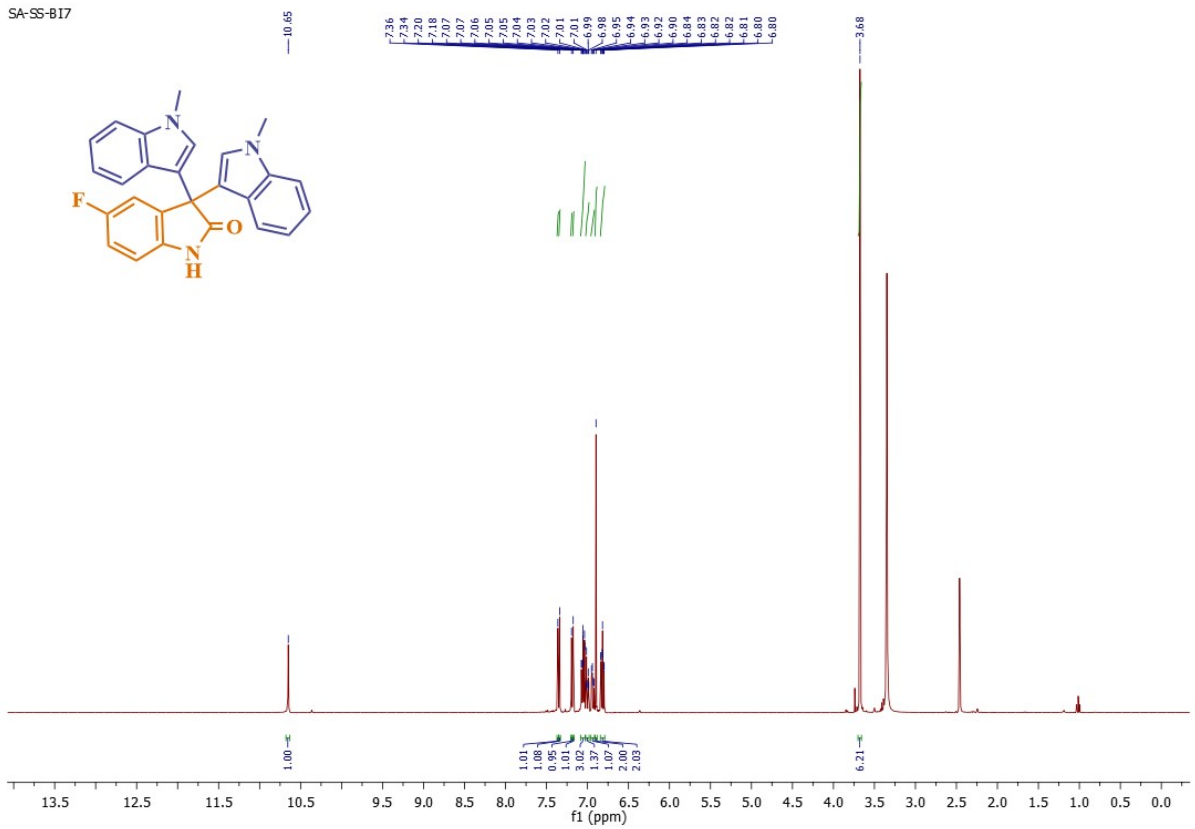


Figure S8: ^{1}H NMR spectrum of compound 5D.

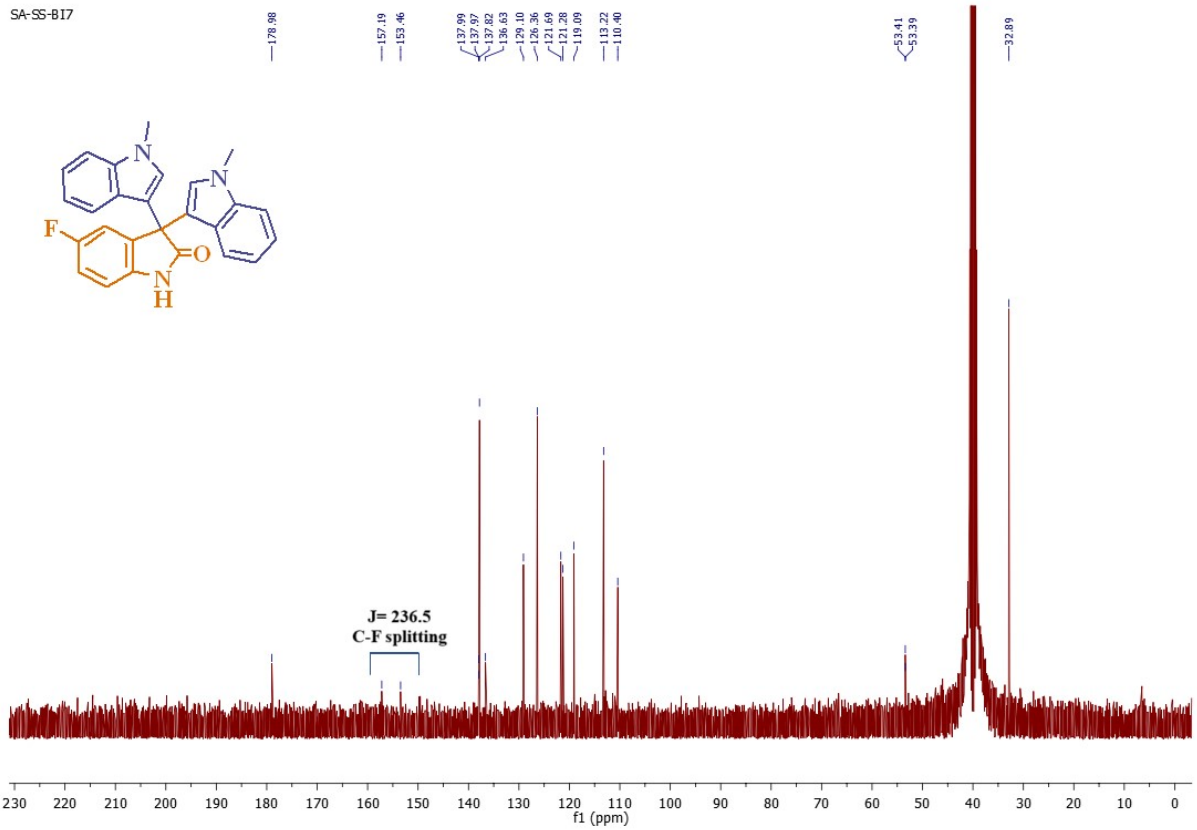


Figure S9: ^{13}C NMR spectrum of compound 5D.

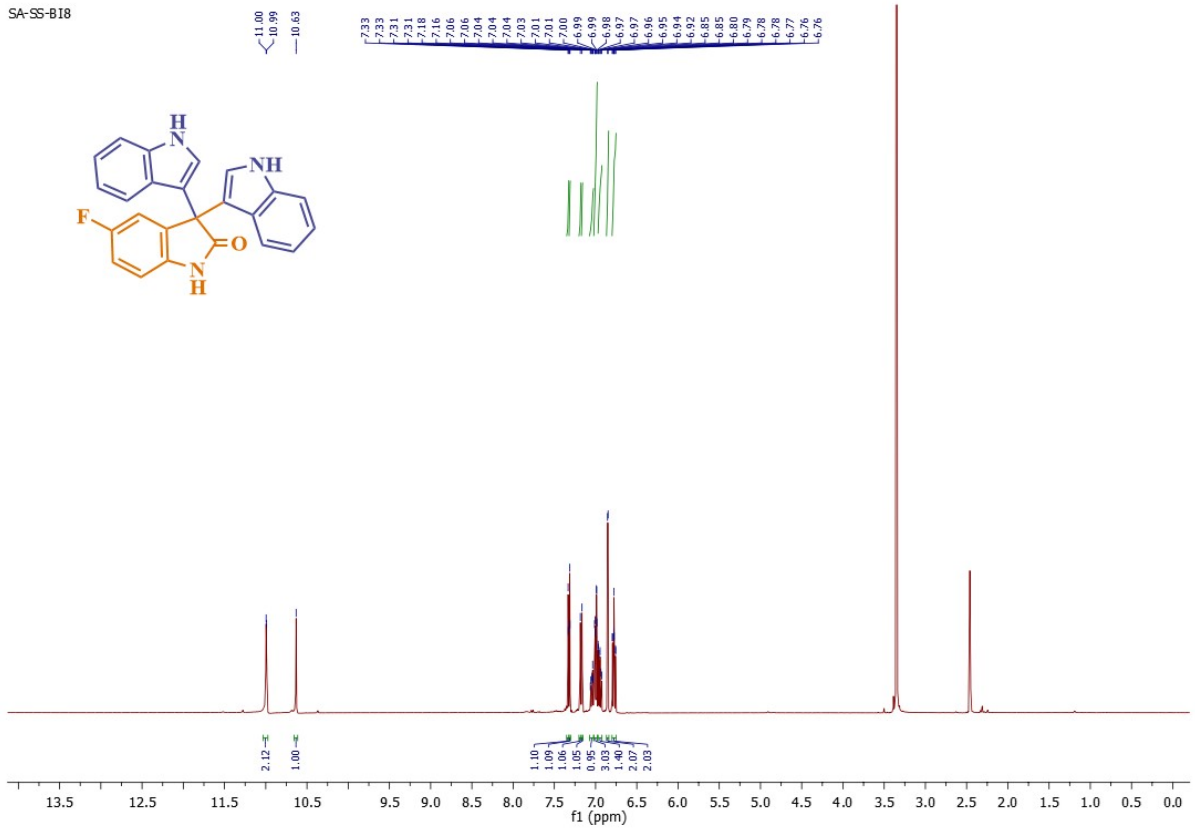


Figure S10: ^{1}H NMR spectrum of compound 5E.

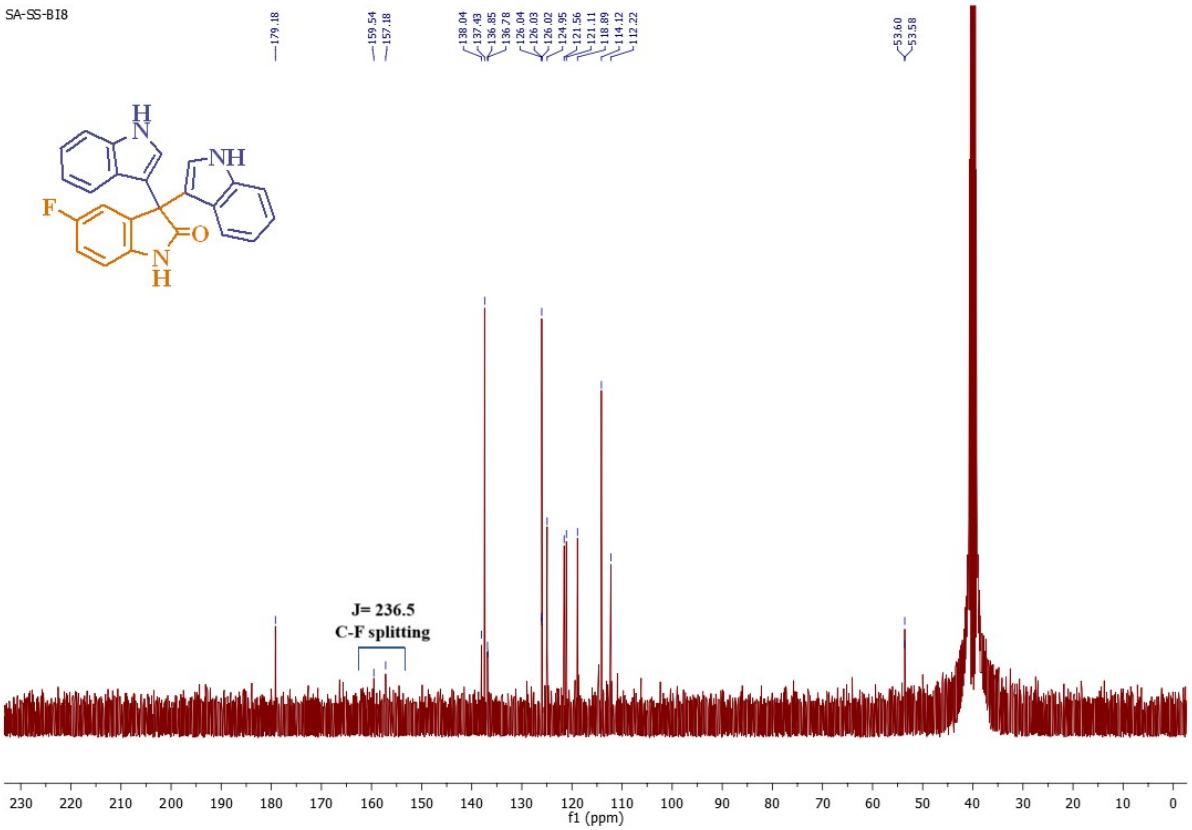


Figure S11: ^{13}C NMR spectrum of compound 5E.

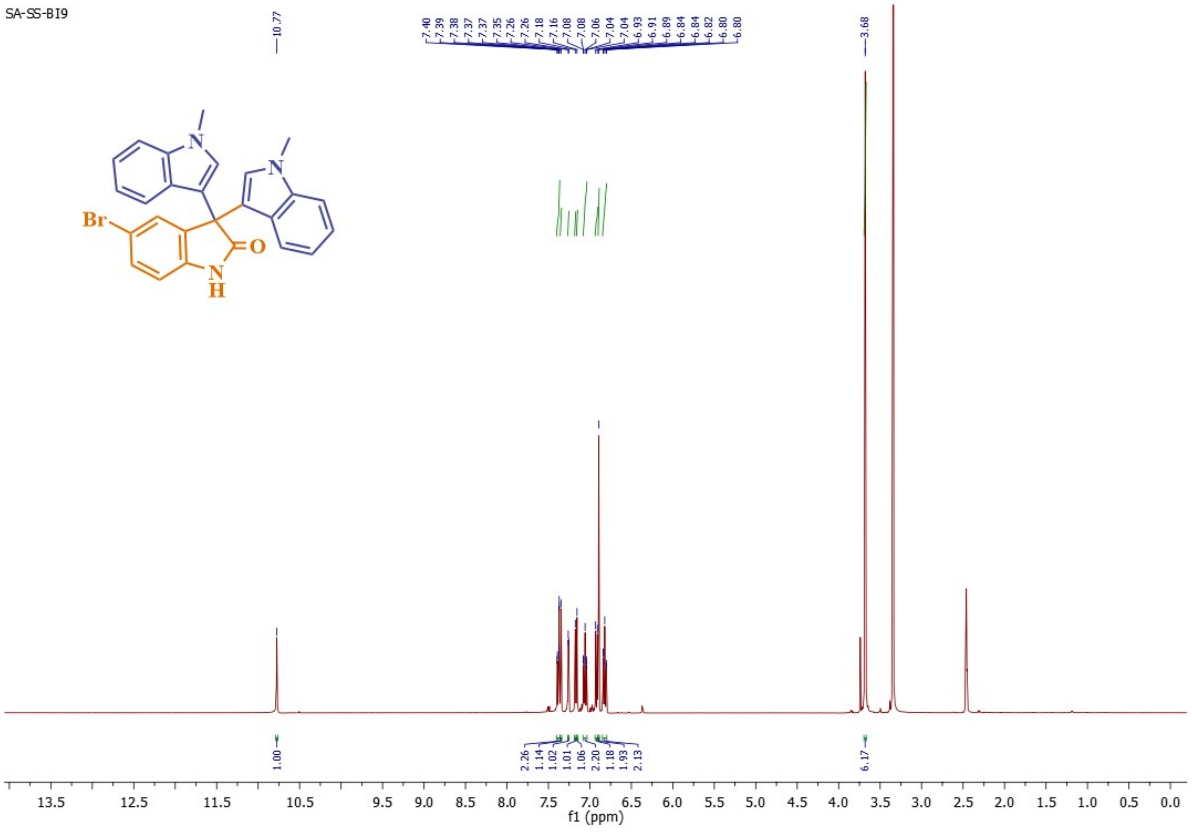


Figure S12: ^{1}H NMR spectrum of compound 5F.

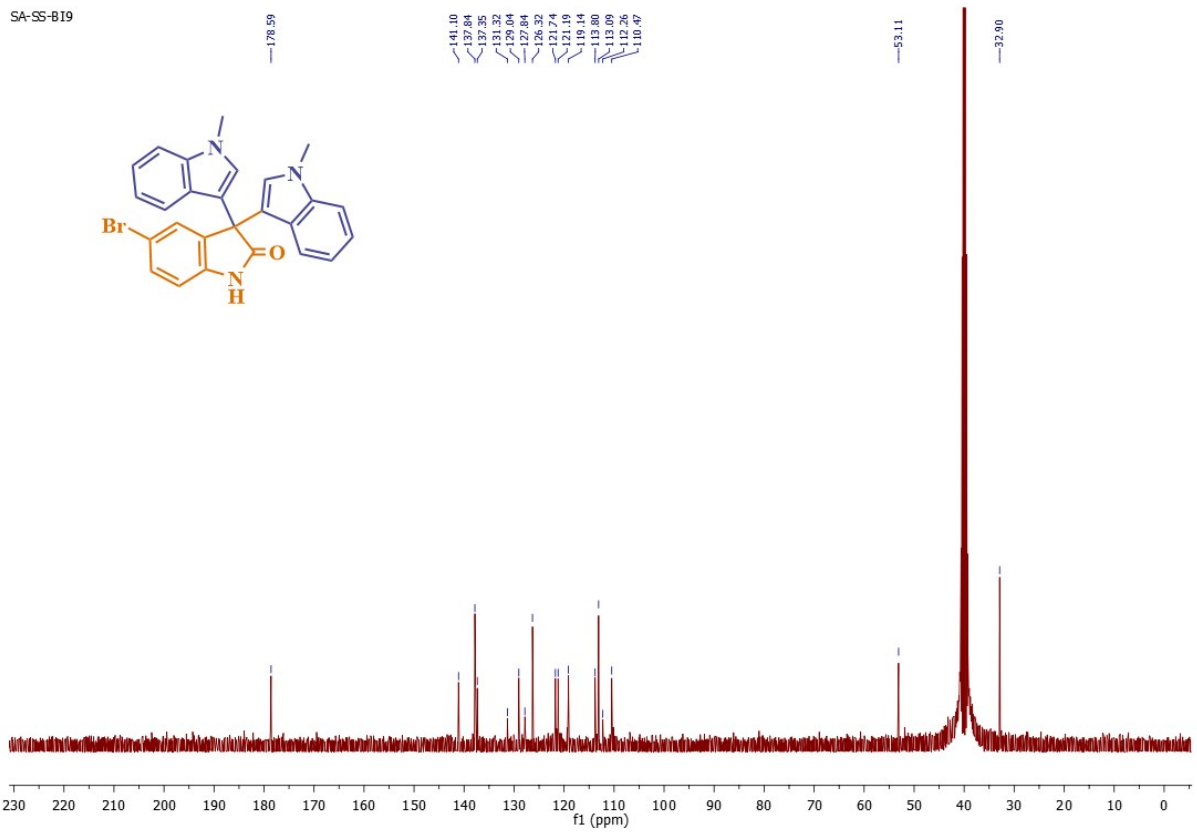


Figure S13: ^{13}C NMR spectrum of compound 5F.

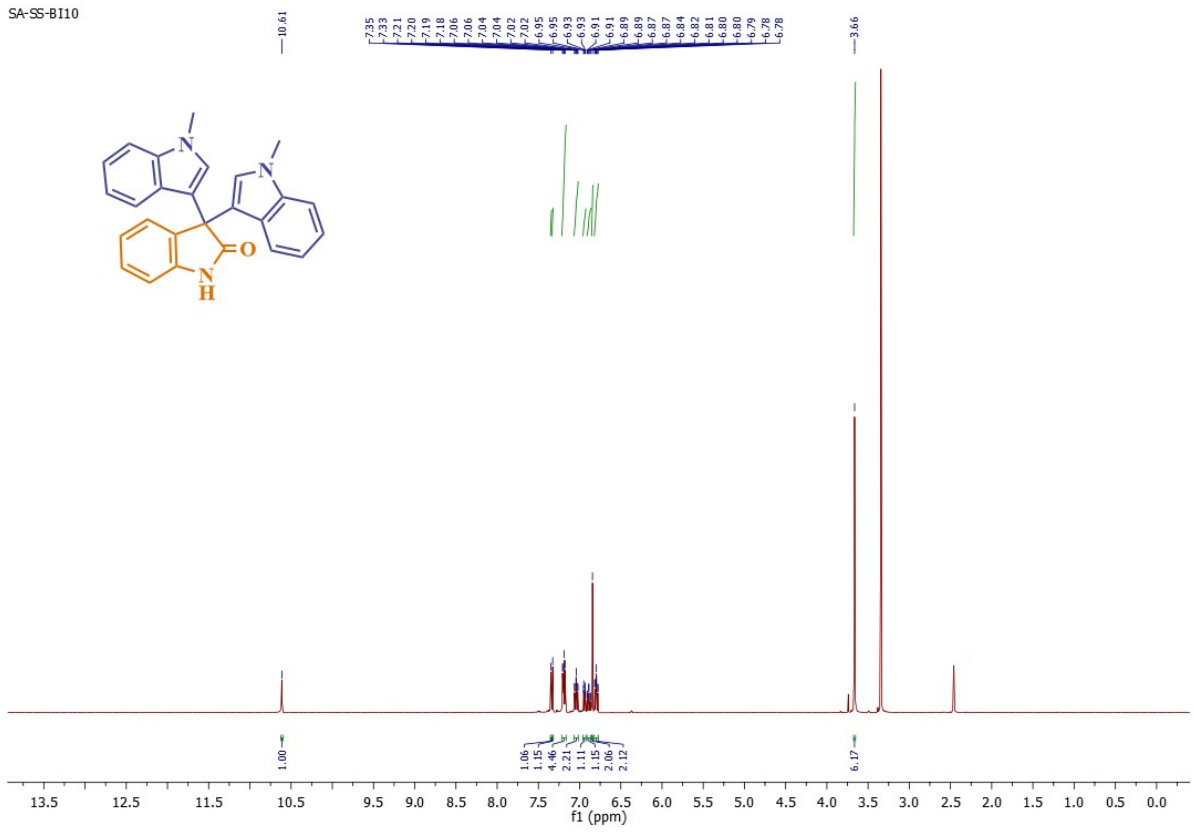


Figure S14: ^{1}H NMR spectrum of compound 5G.

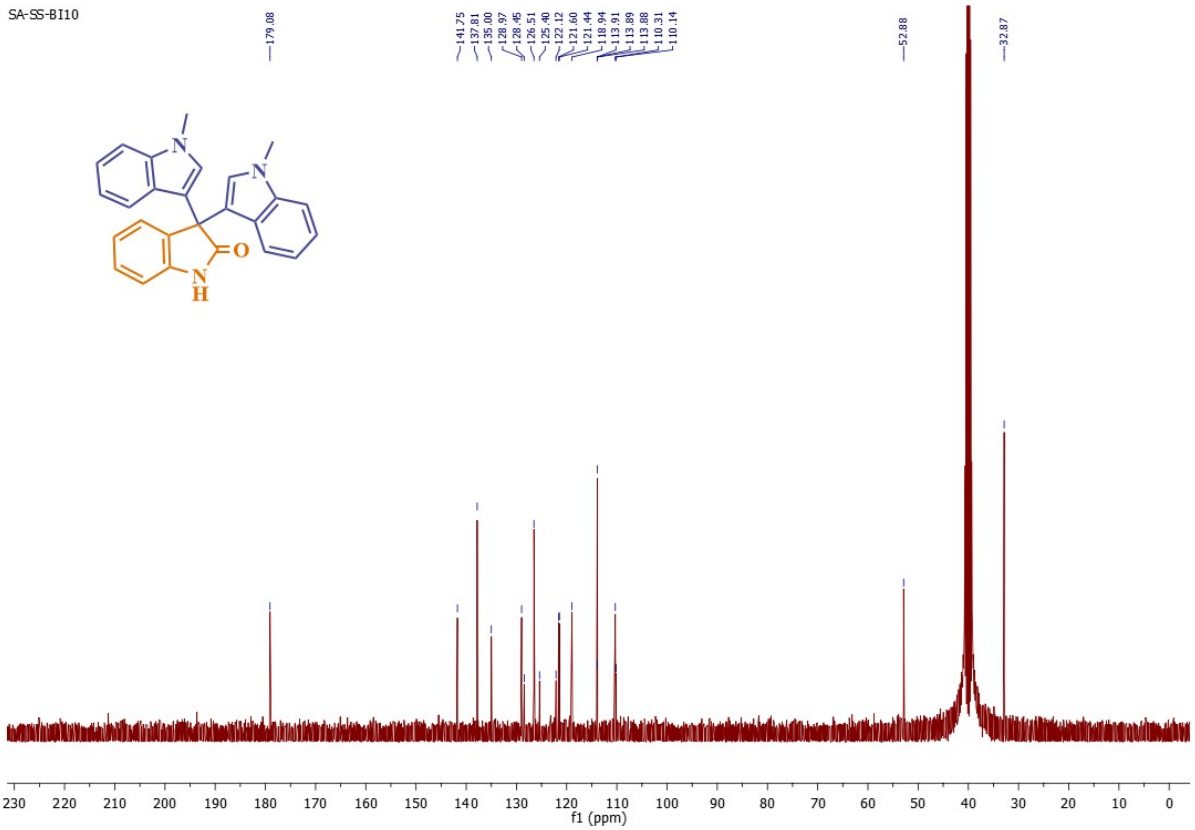


Figure S15: ^{13}C NMR spectrum of compound 5G.

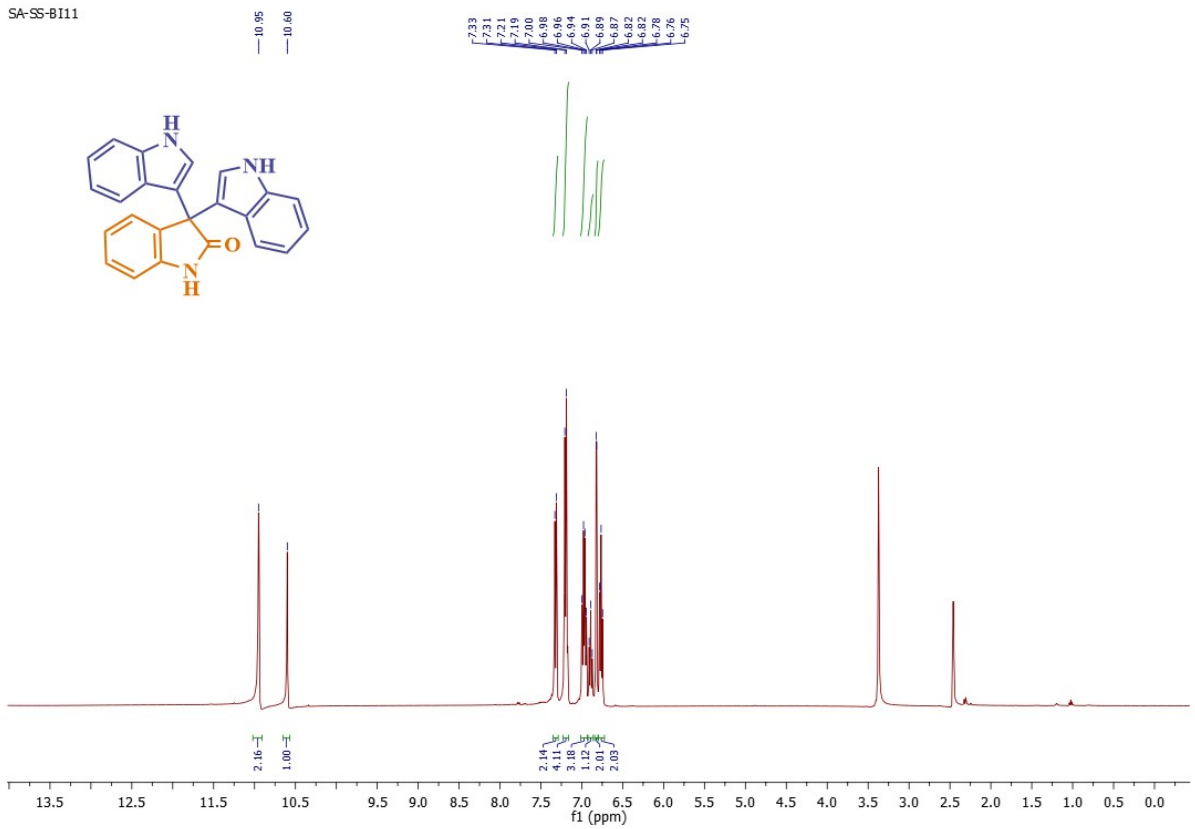


Figure S16: ^{1}H NMR spectrum of compound 5H.

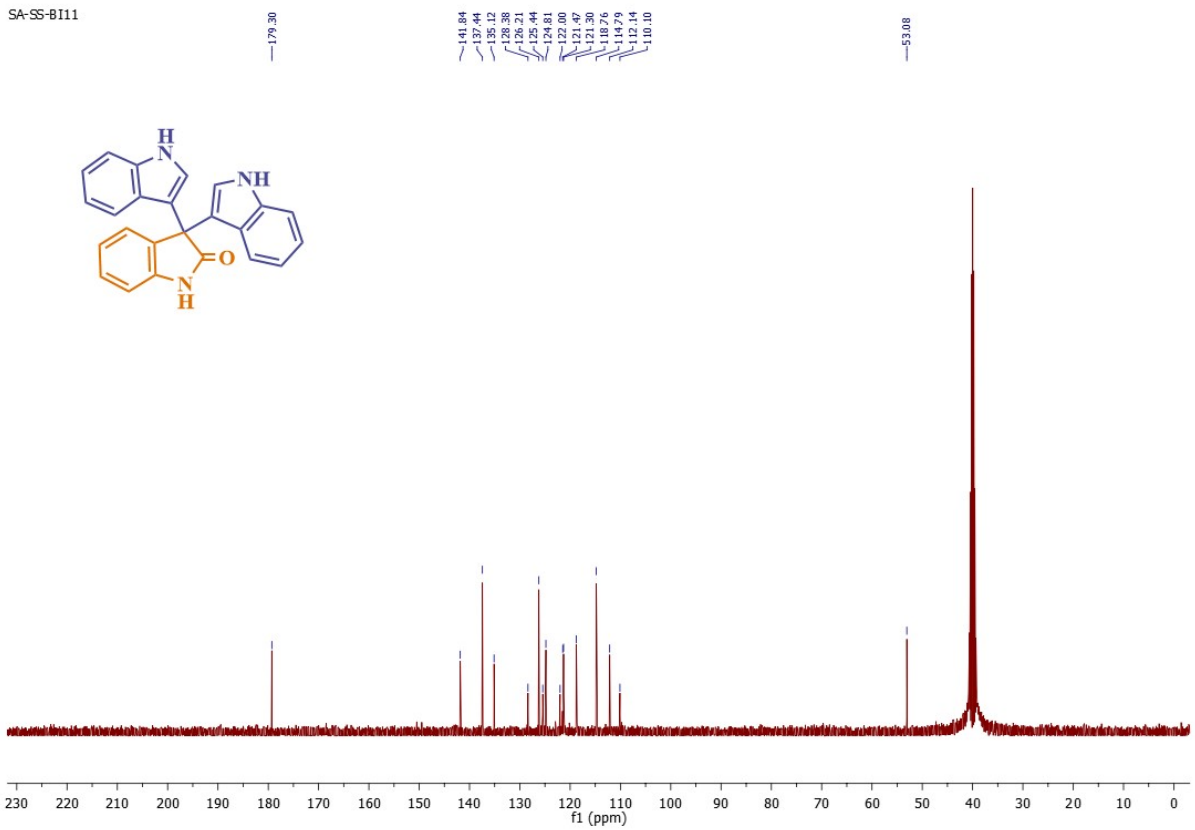


Figure S17: ^{13}C NMR spectrum of compound 5H.

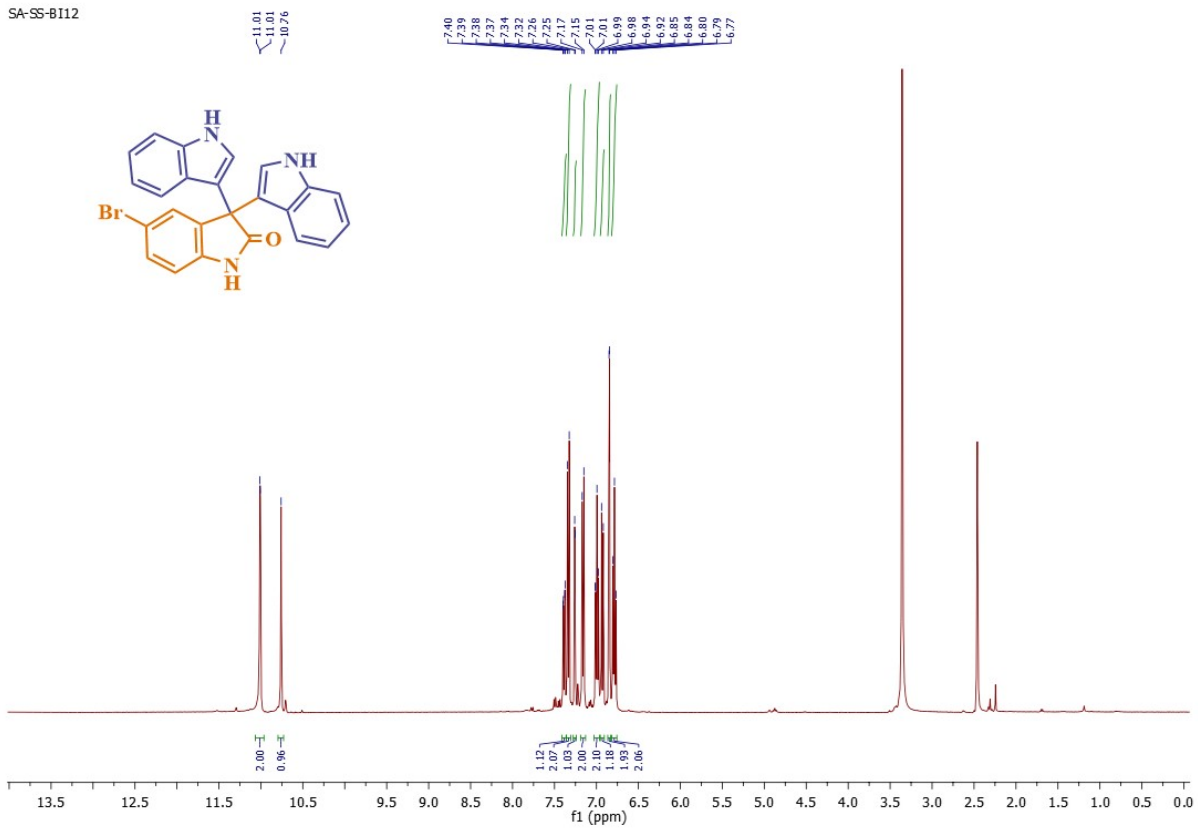


Figure S18: ^{1}H NMR spectrum of compound 5I.

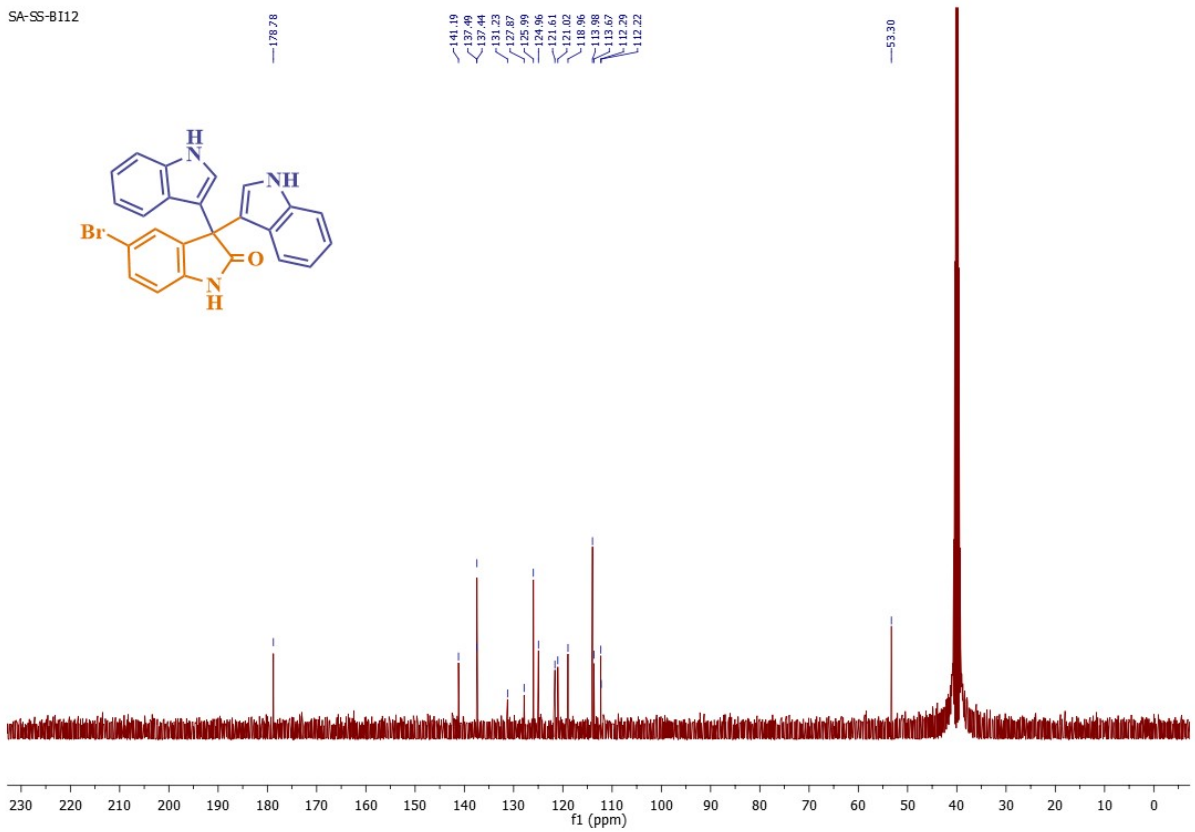


Figure S19: ^{13}C NMR spectrum of compound 5I.

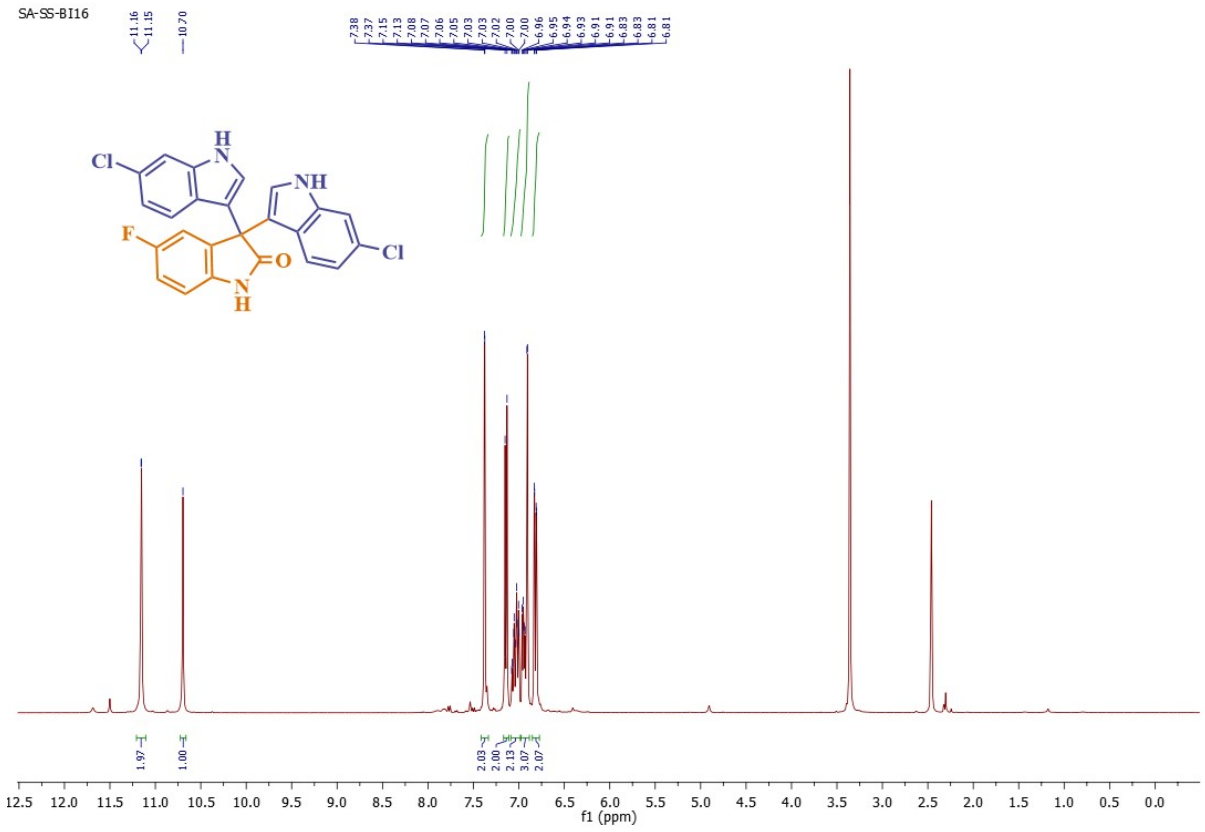


Figure S20: ^{1}H NMR spectrum of compound 5J.

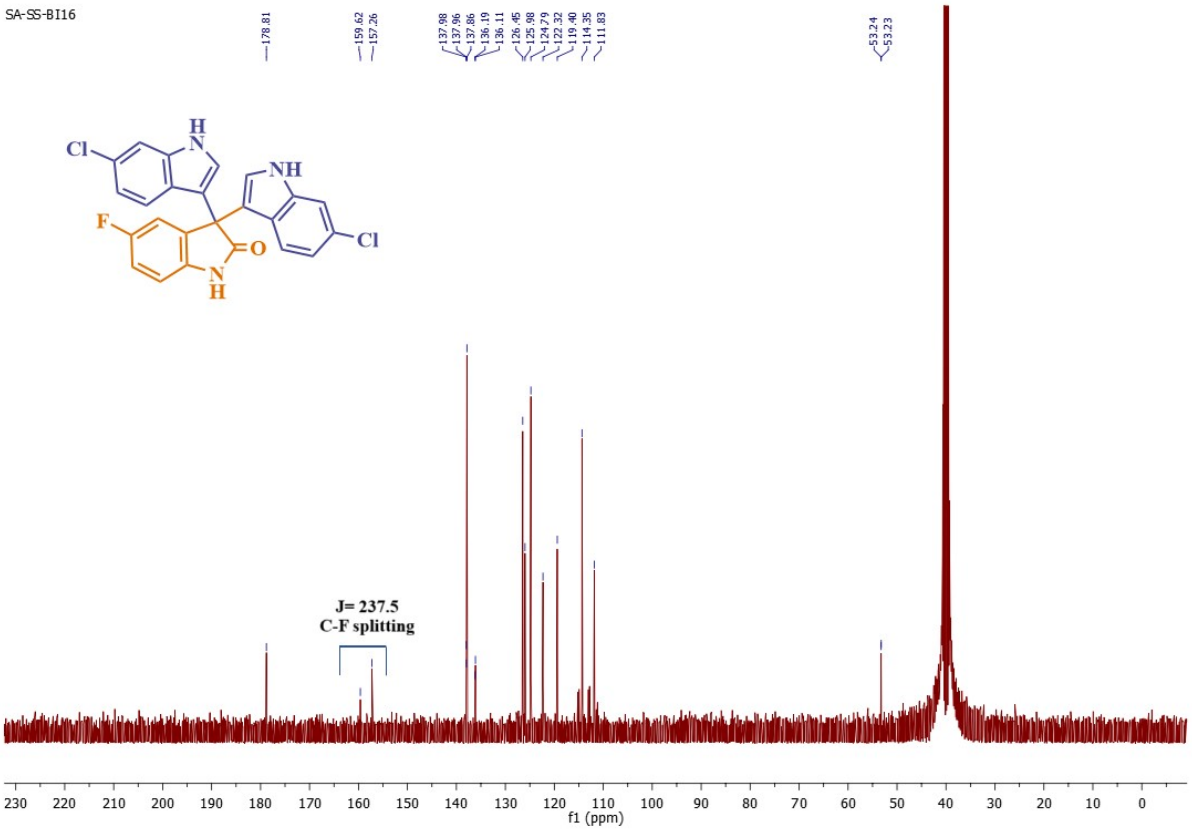


Figure S21: ^{13}C NMR spectrum of compound 5J.

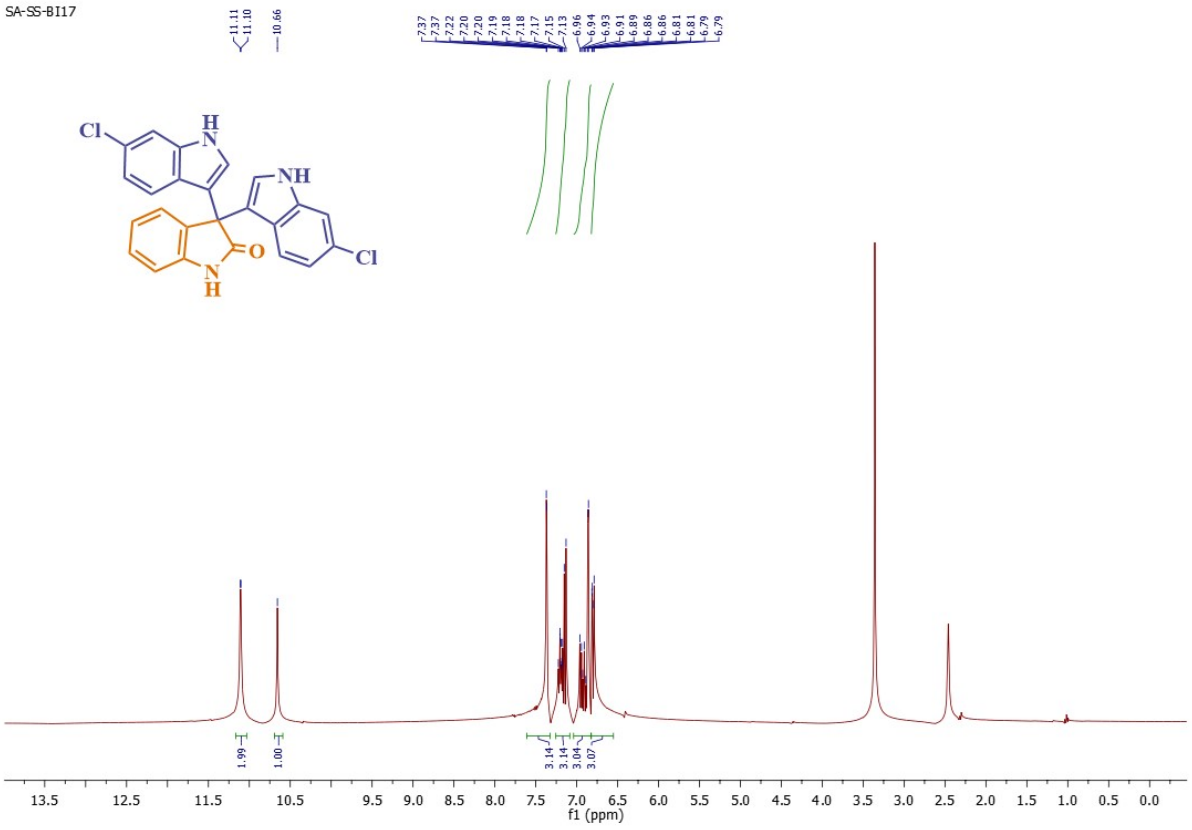


Figure S22: ^{1}H NMR spectrum of compound 5K.

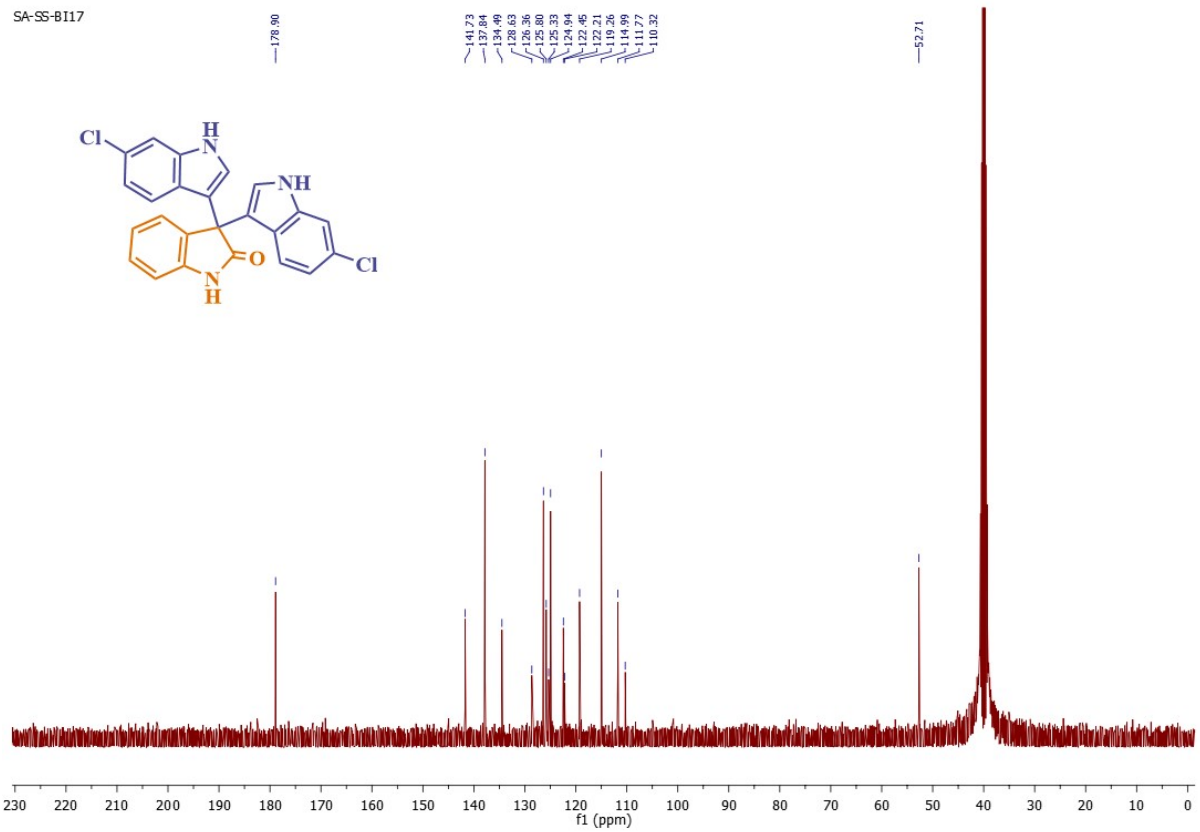


Figure S23: ^{13}C NMR spectrum of compound 5K.

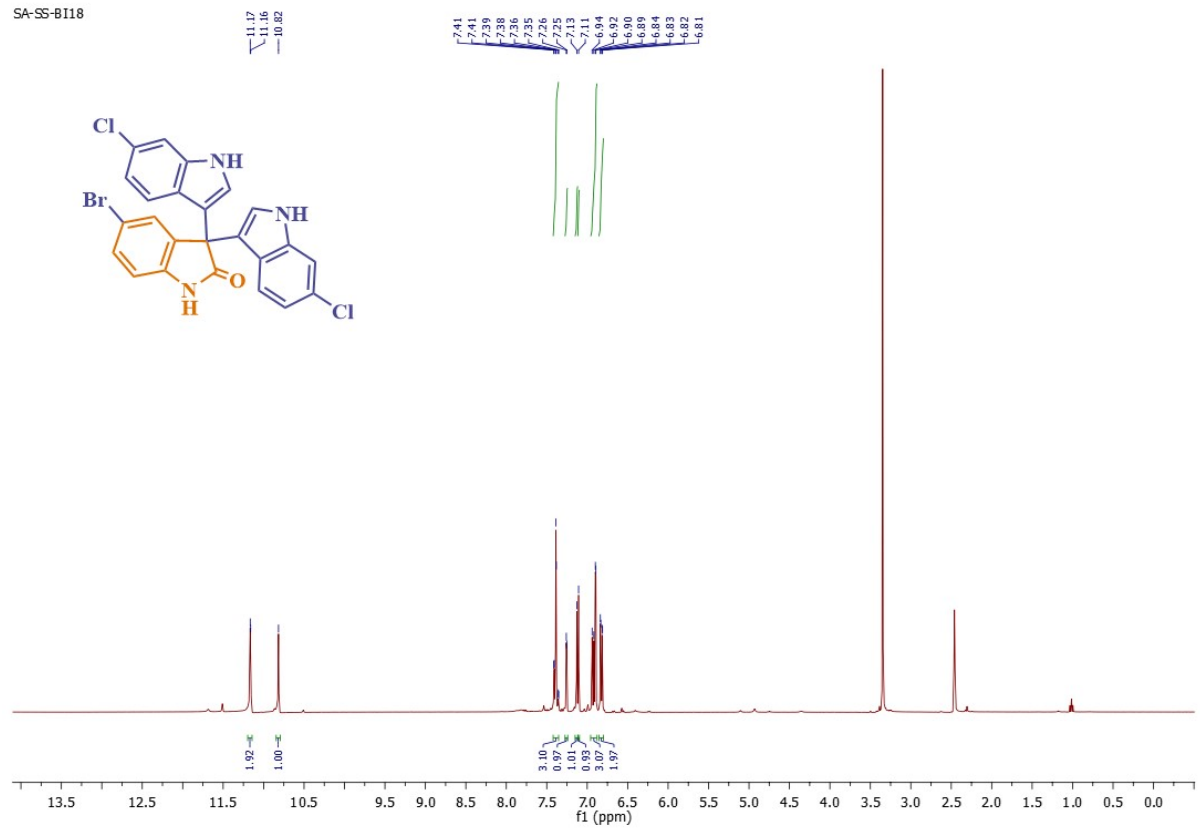


Figure S24: ^{1}H NMR spectrum of compound 5L.

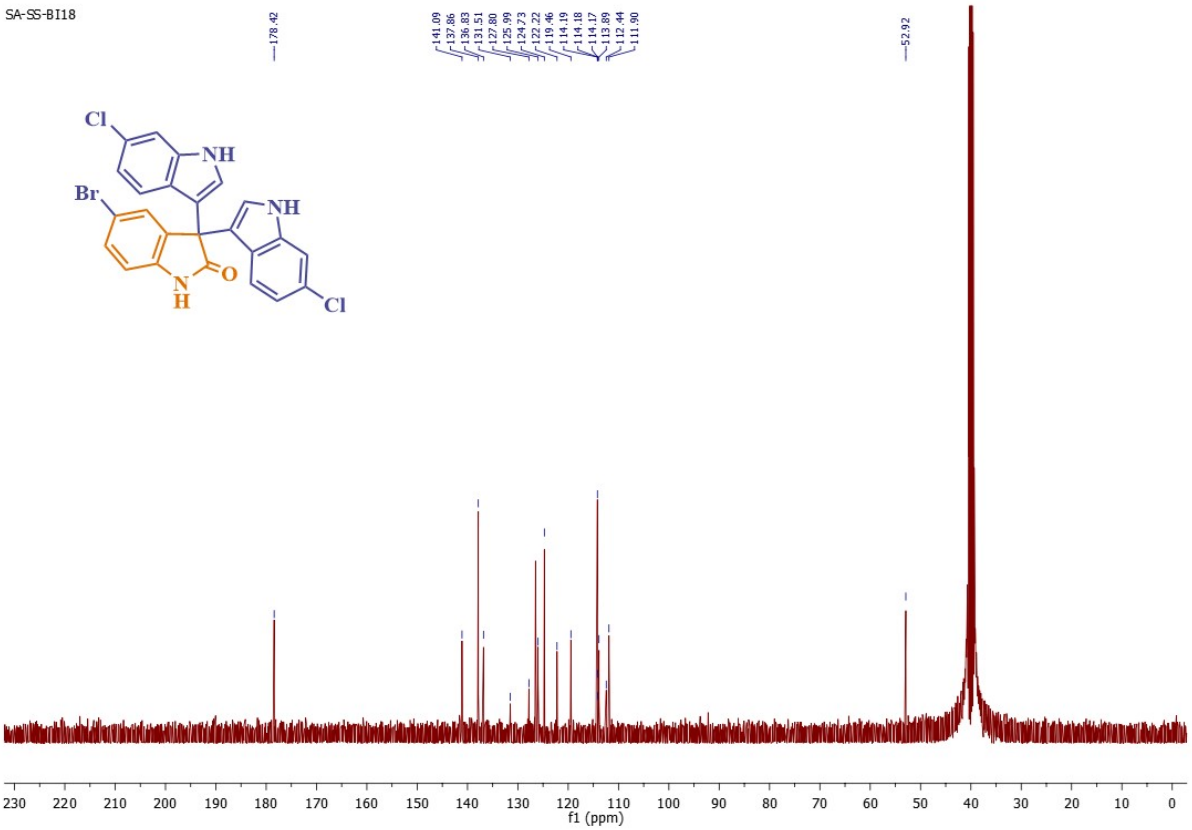


Figure S25: ^{13}C NMR spectrum of compound 5L.

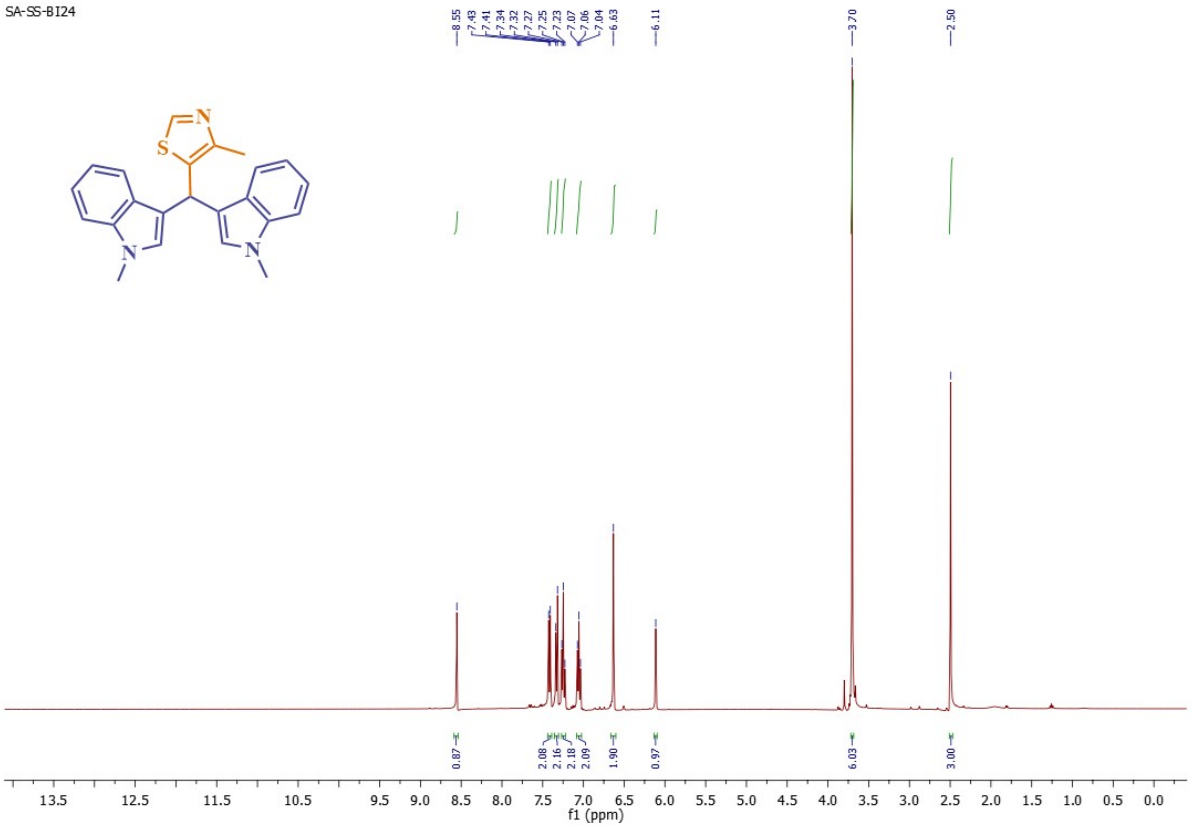


Figure S26: ^{1}H NMR spectrum of compound 5M.

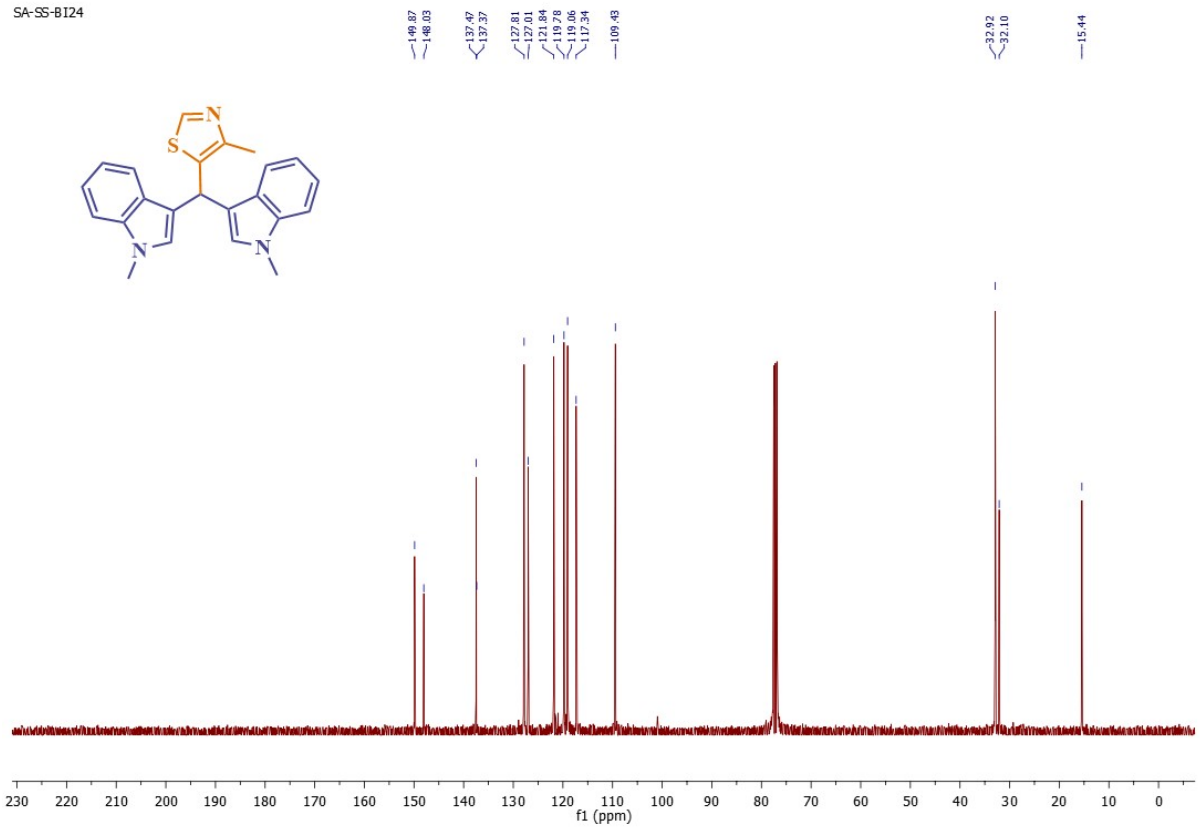


Figure S27: ^{13}C NMR spectrum of compound5M.

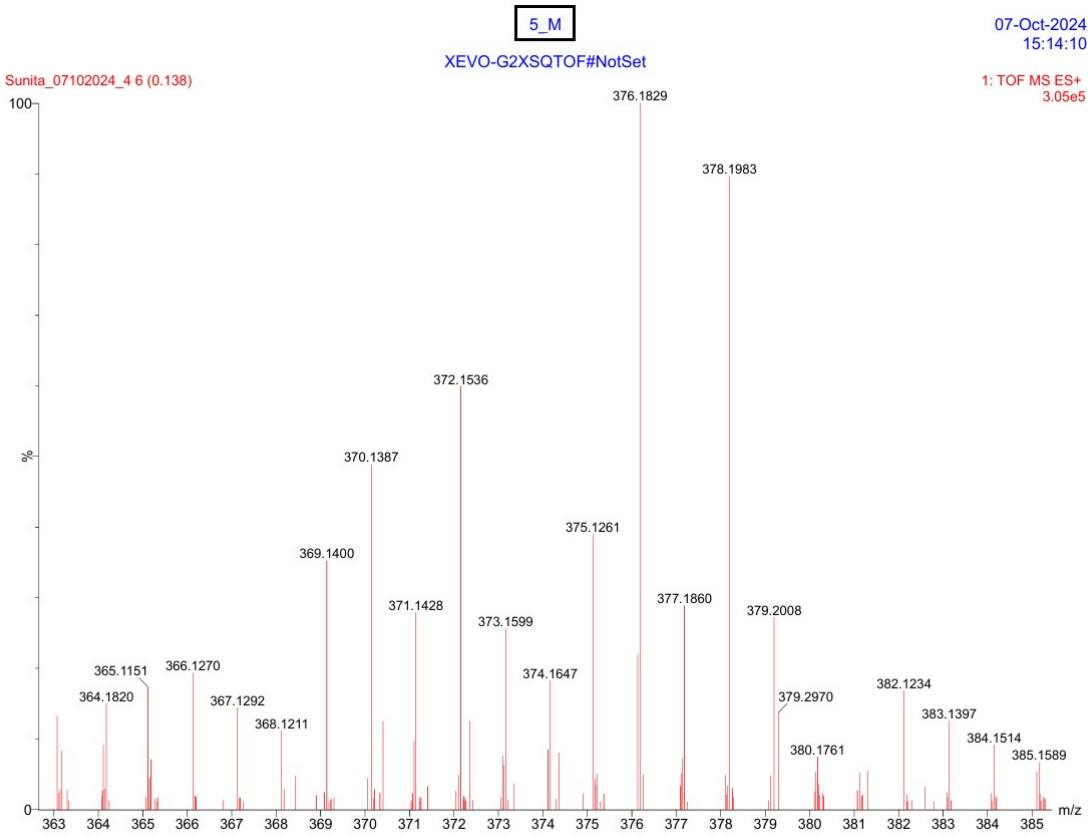


Figure S28: The HRMS profile of compound 5M.

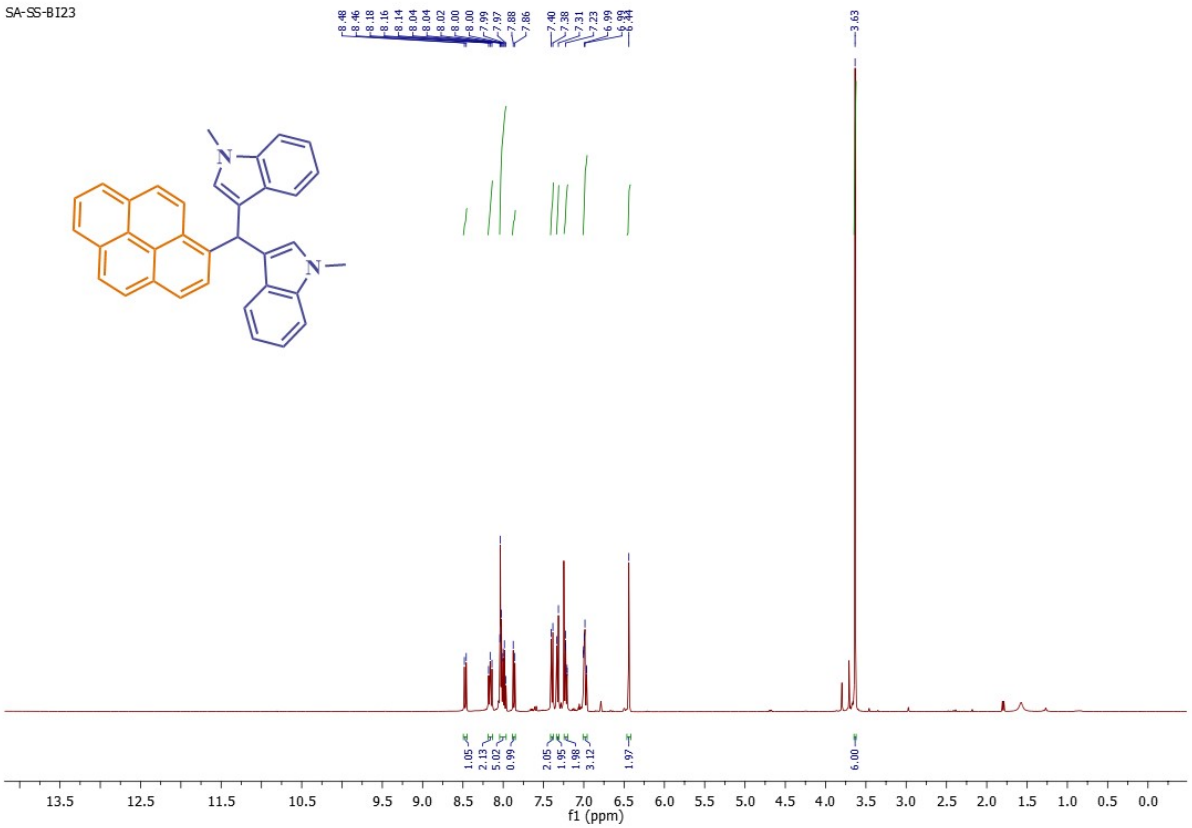


Figure S29: ^{1}H NMR spectrum of compound 5N.

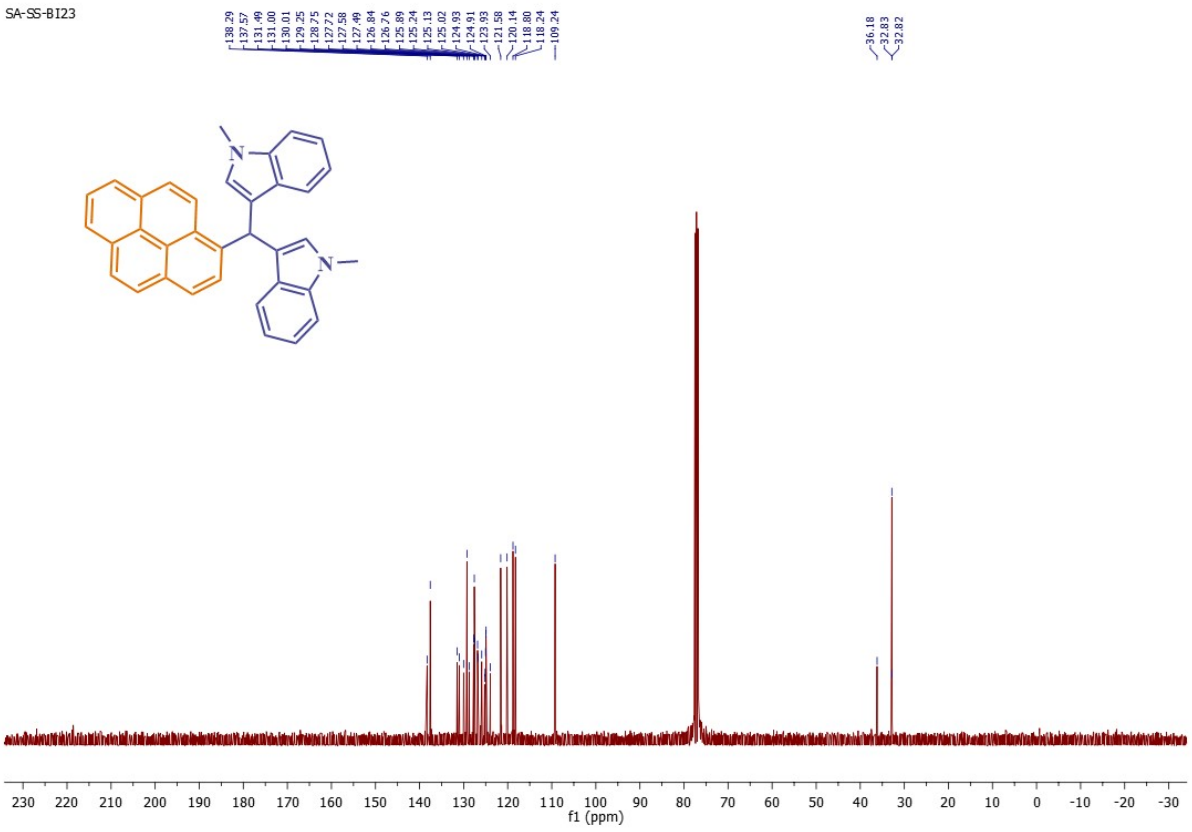


Figure S30: ^{13}C NMR spectrum of compound 5N.

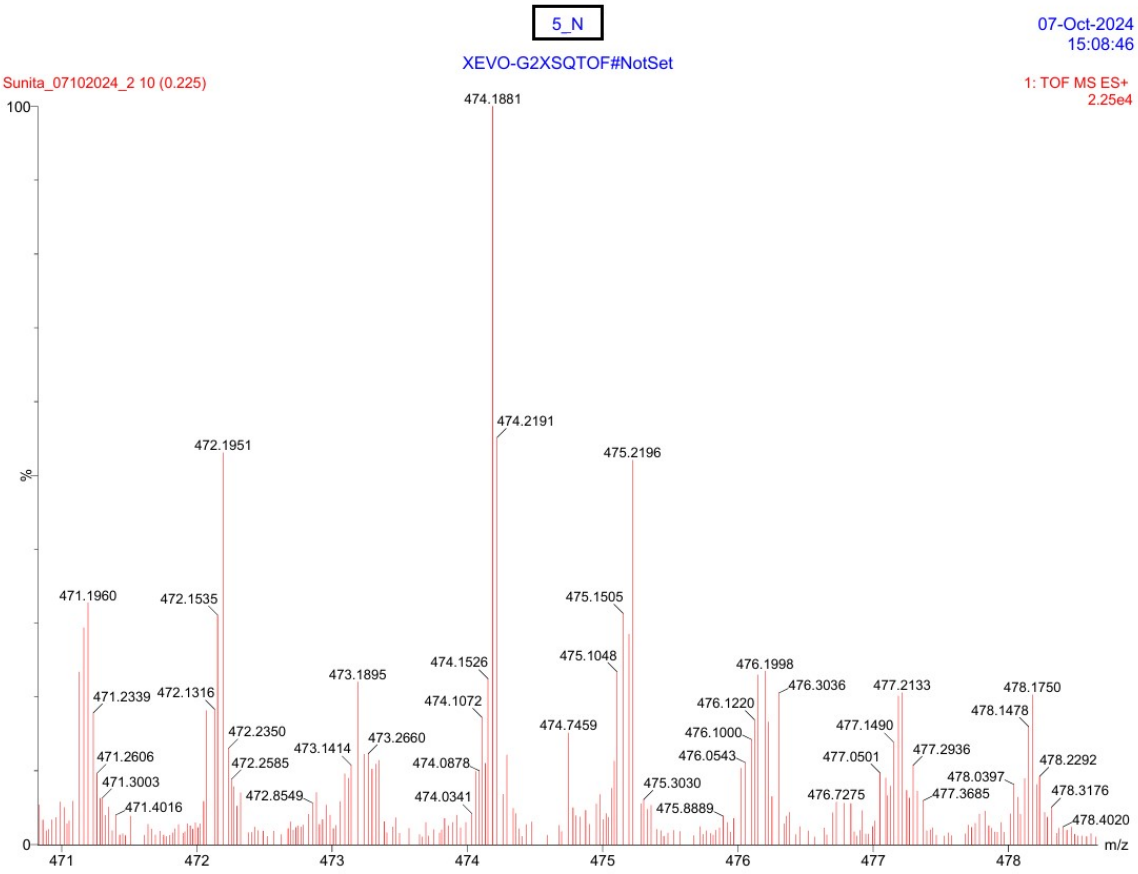


Figure S31: The HRMS profile of compound 5N.

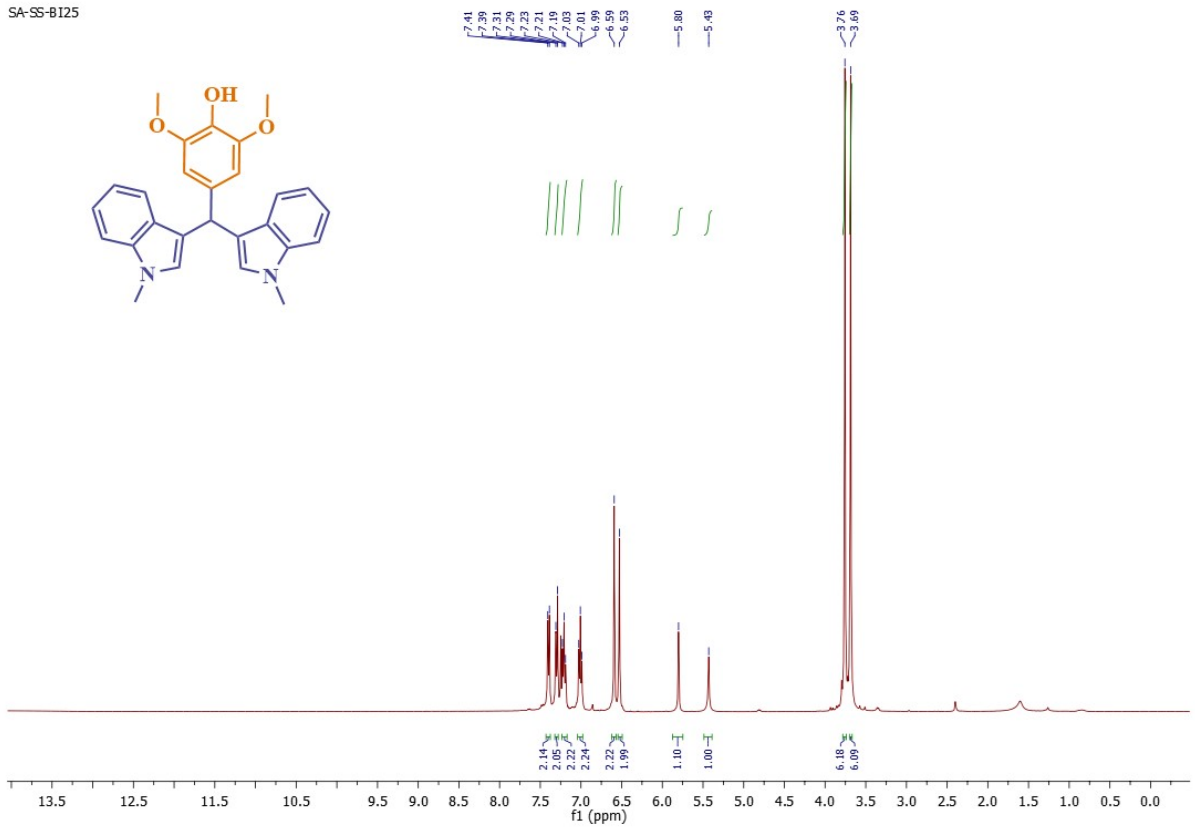


Figure S32: ^{1}H NMR spectrum of compound 5O.

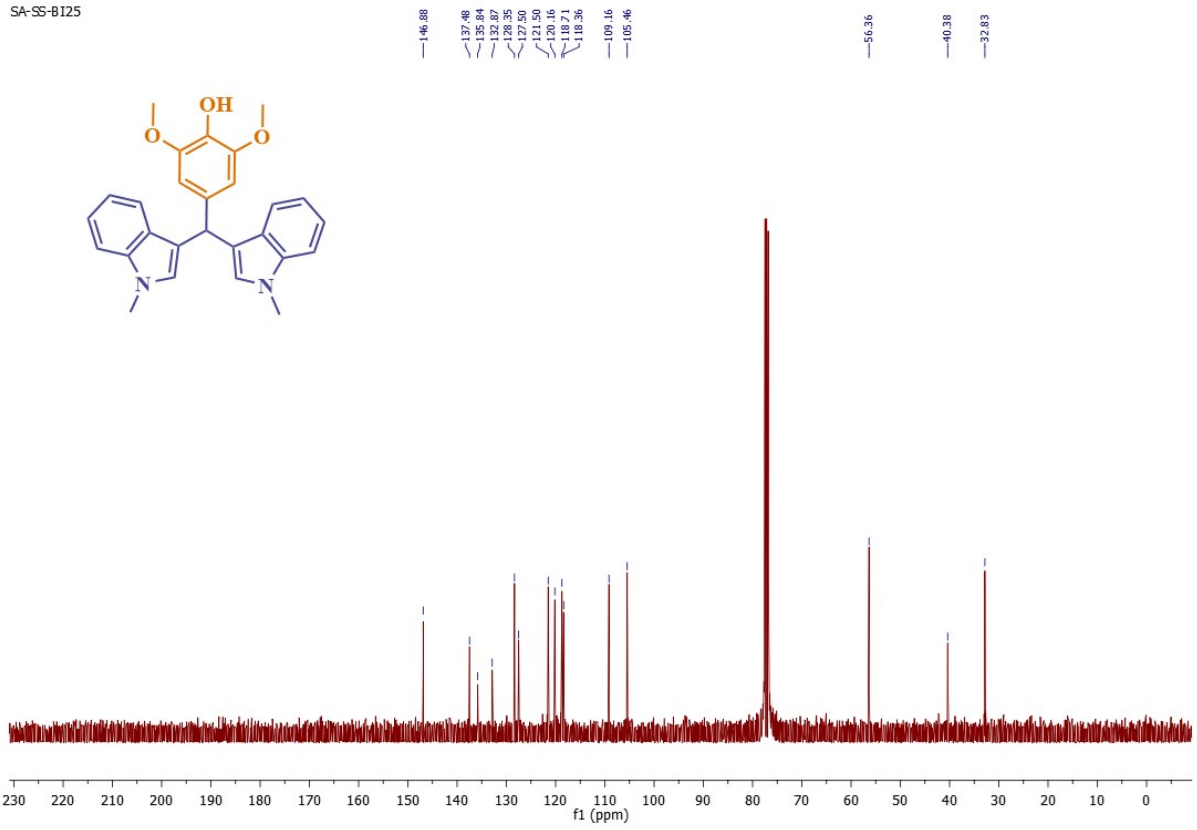


Figure S33: ^{13}C NMR spectrum of compound 5O.

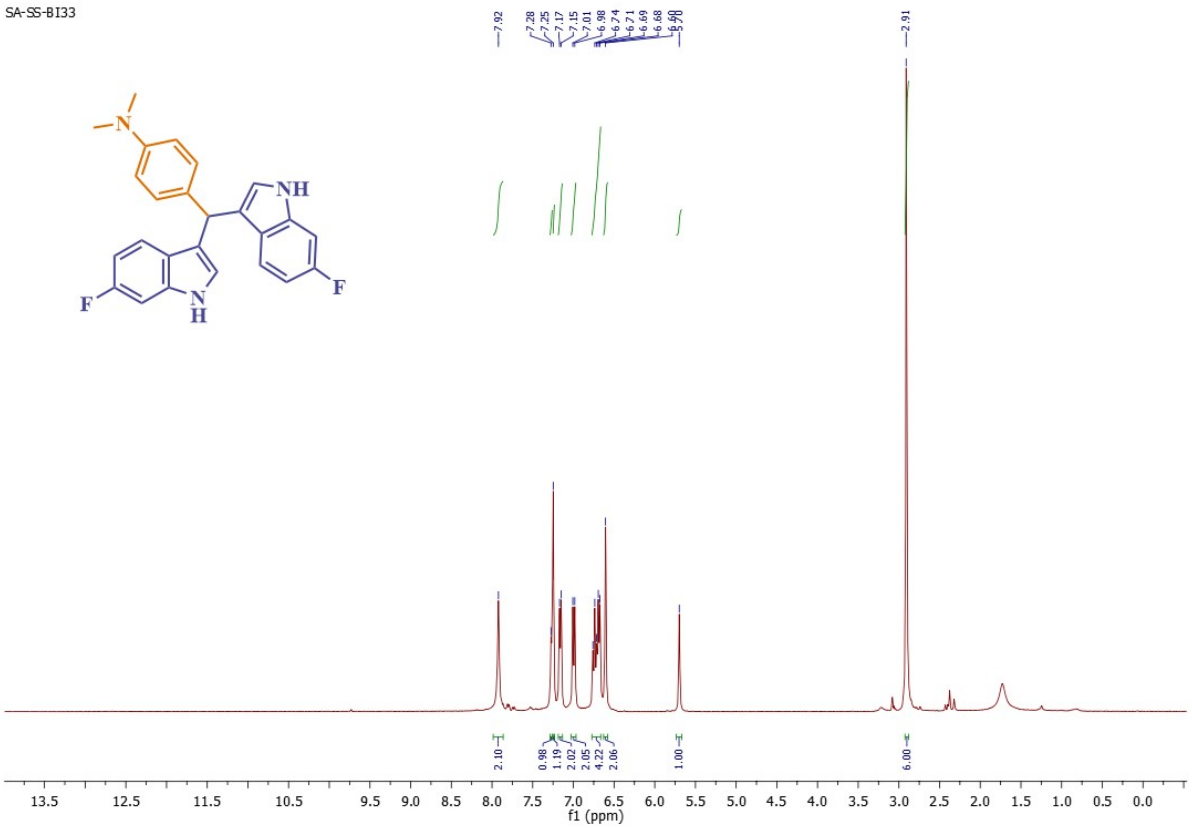


Figure S34: ^{1}H NMR spectrum of compound 5P.

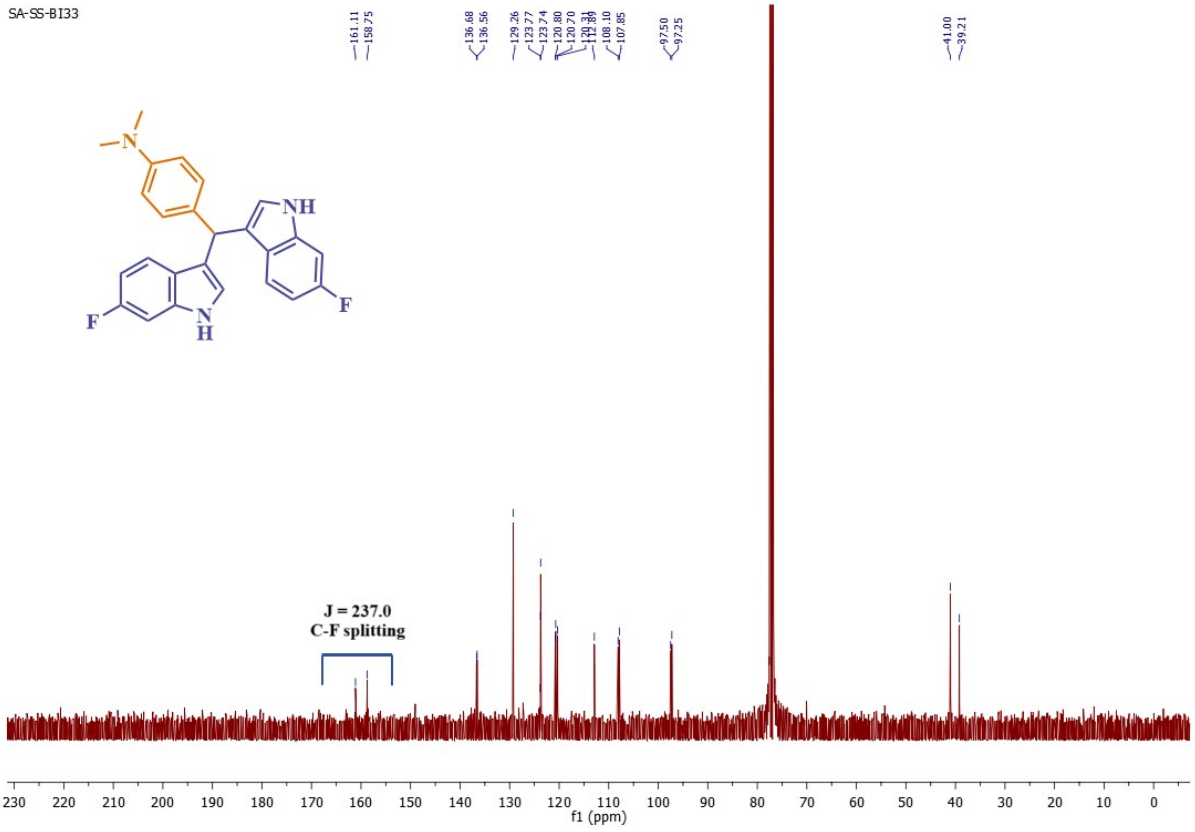


Figure S35: ^{13}C NMR spectrum of compound 5P.

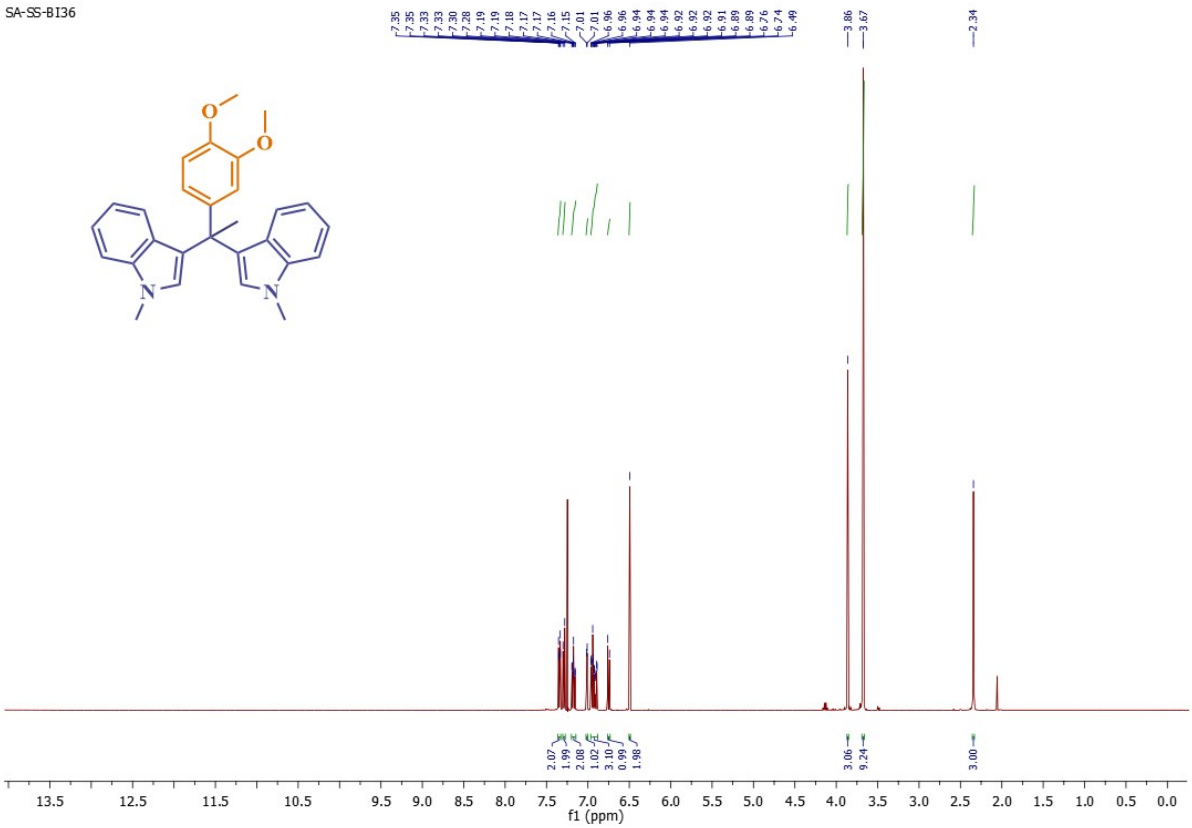


Figure S36: ^{1}H NMR spectrum of compound 5Q.

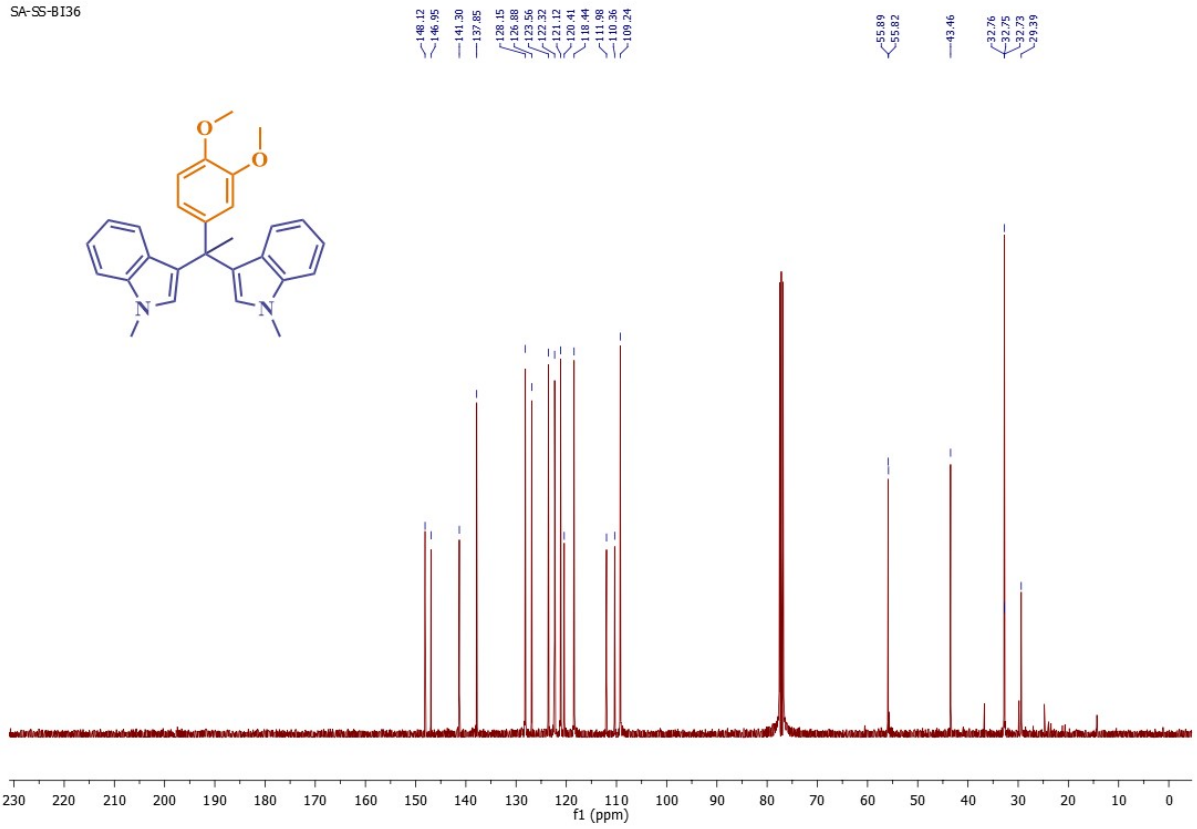


Figure S37: ^{13}C NMR spectrum of compound 5Q.

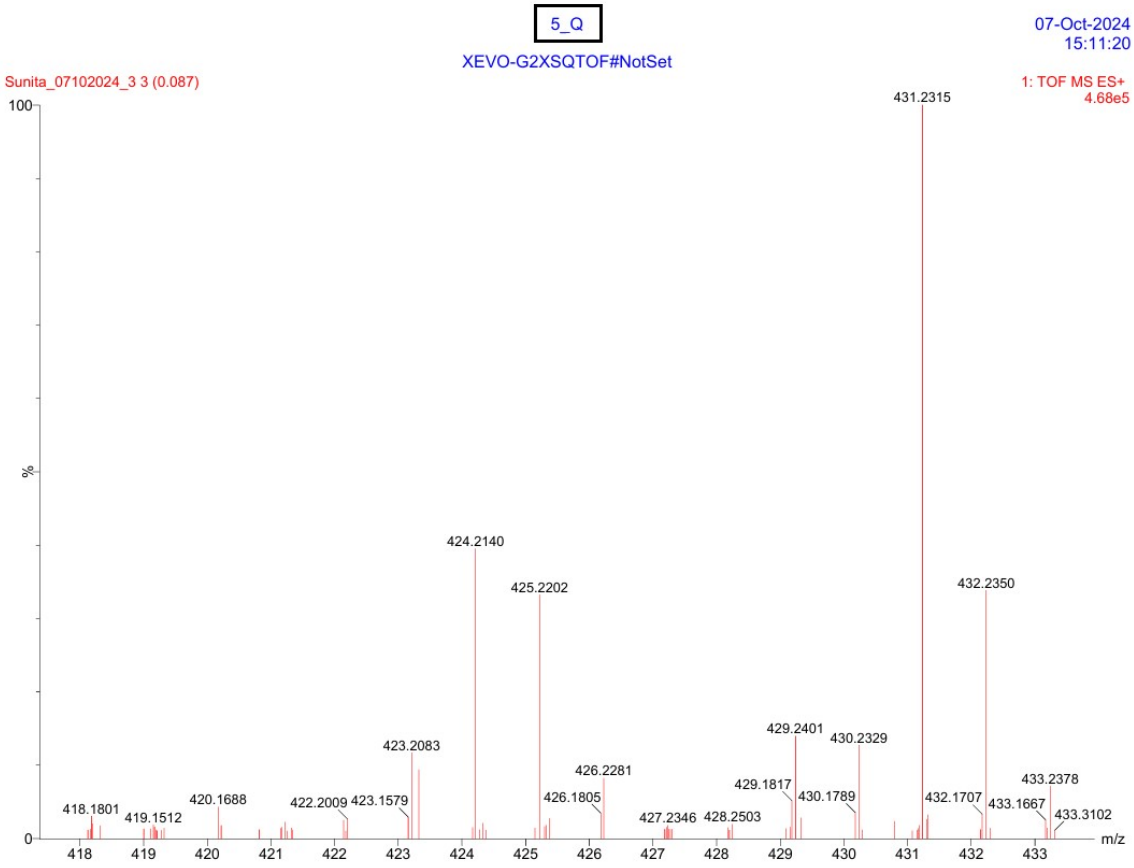


Figure S38: The HRMS profile of compound 5Q.

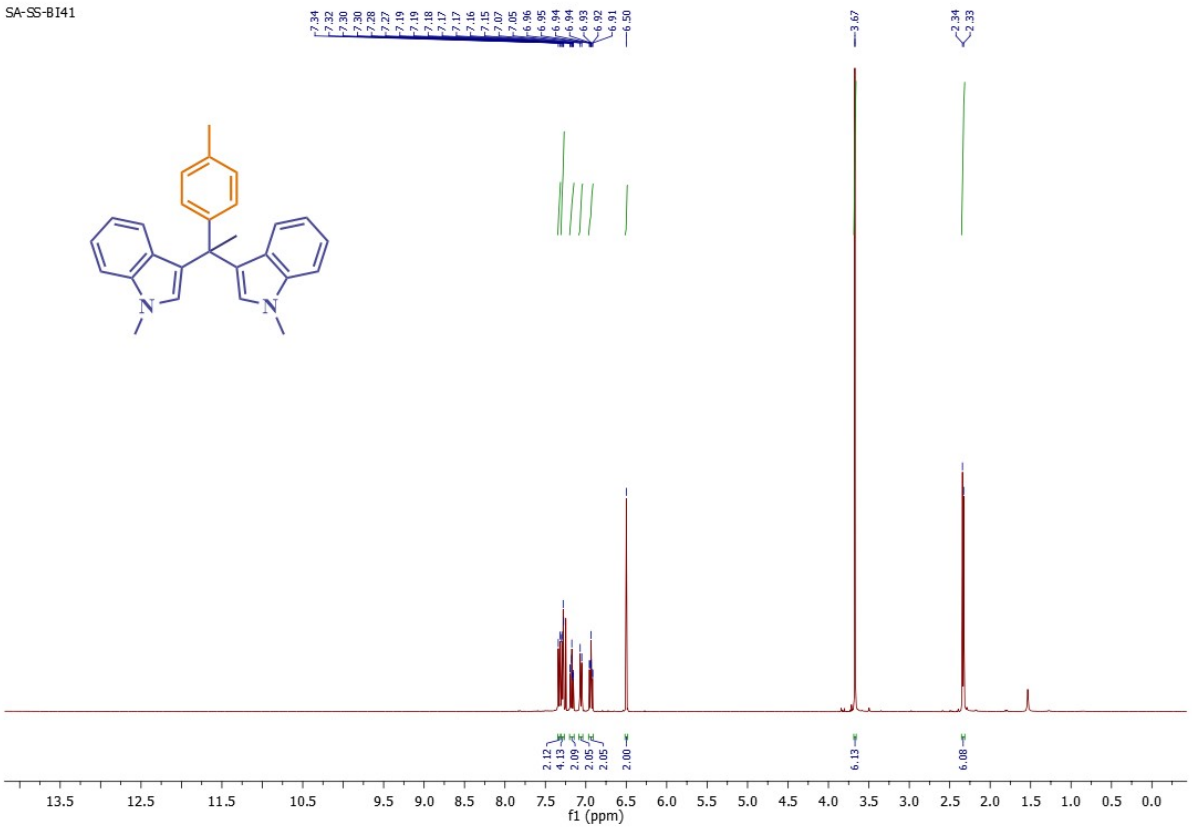


Figure S39: ^{1}H NMR spectrum of compound 5R.

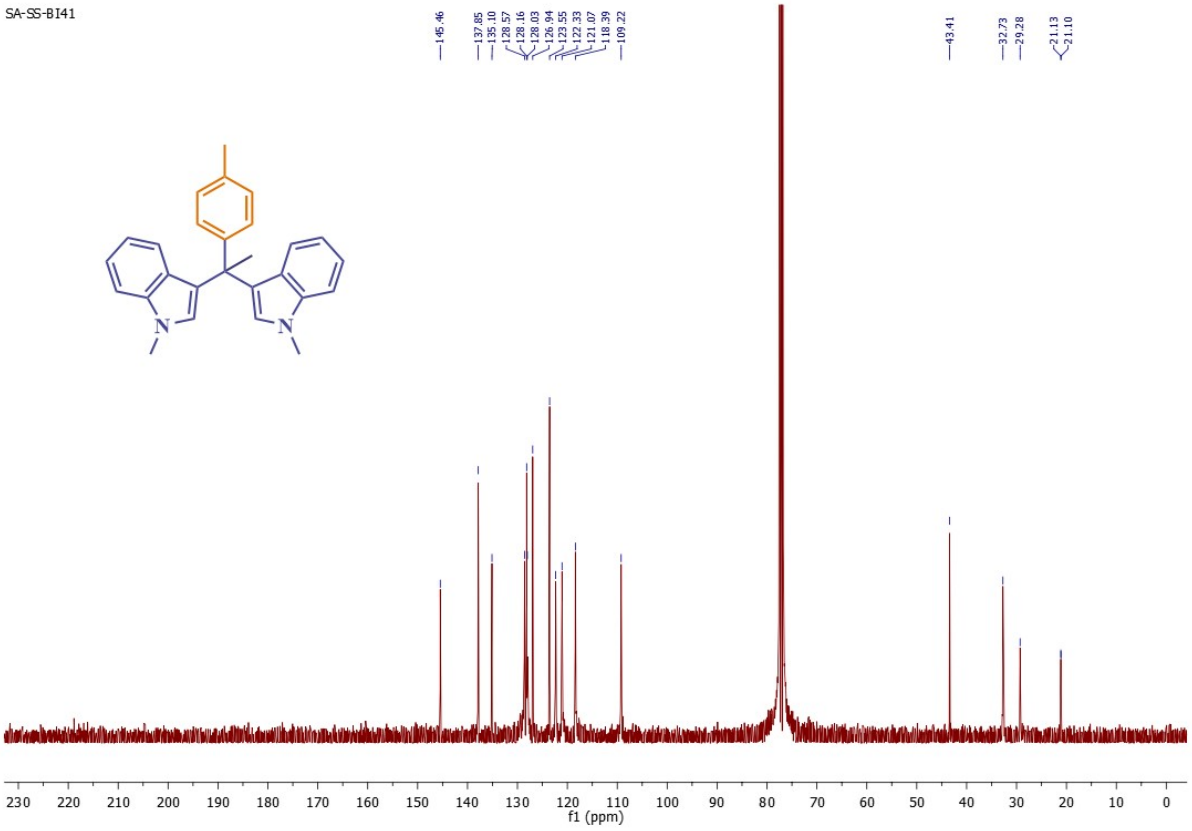


Figure S40: ^{13}C NMR spectrum of compound 5R.

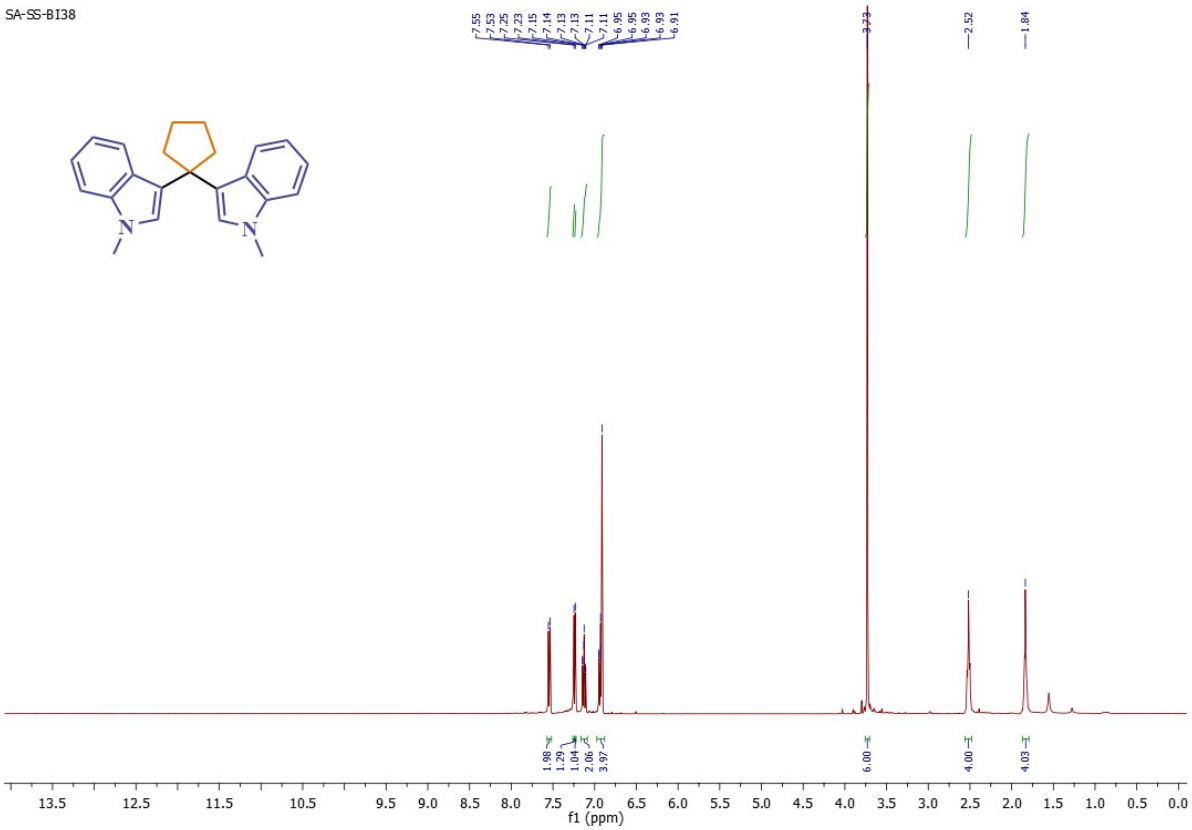


Figure S41: ^{1}H NMR spectrum of compound 5S.

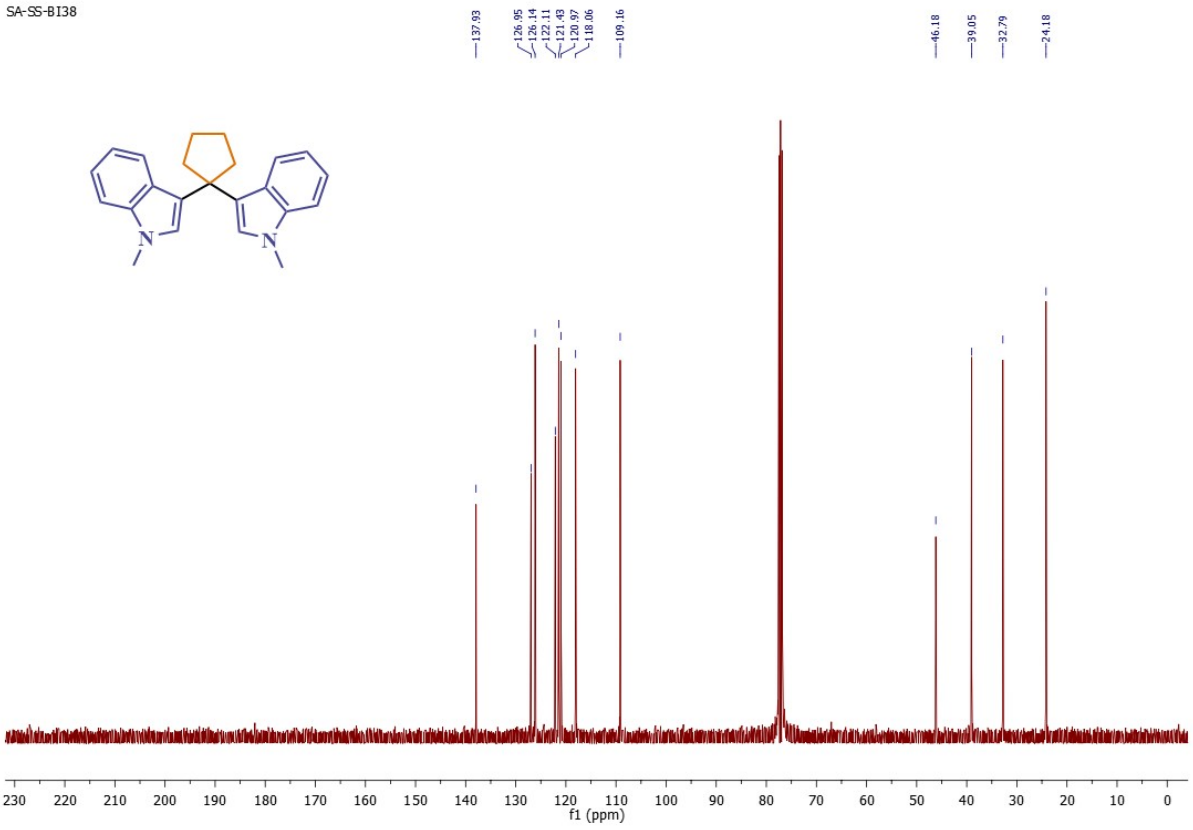


Figure S42: ^{13}C NMR spectrum of compound 5S.

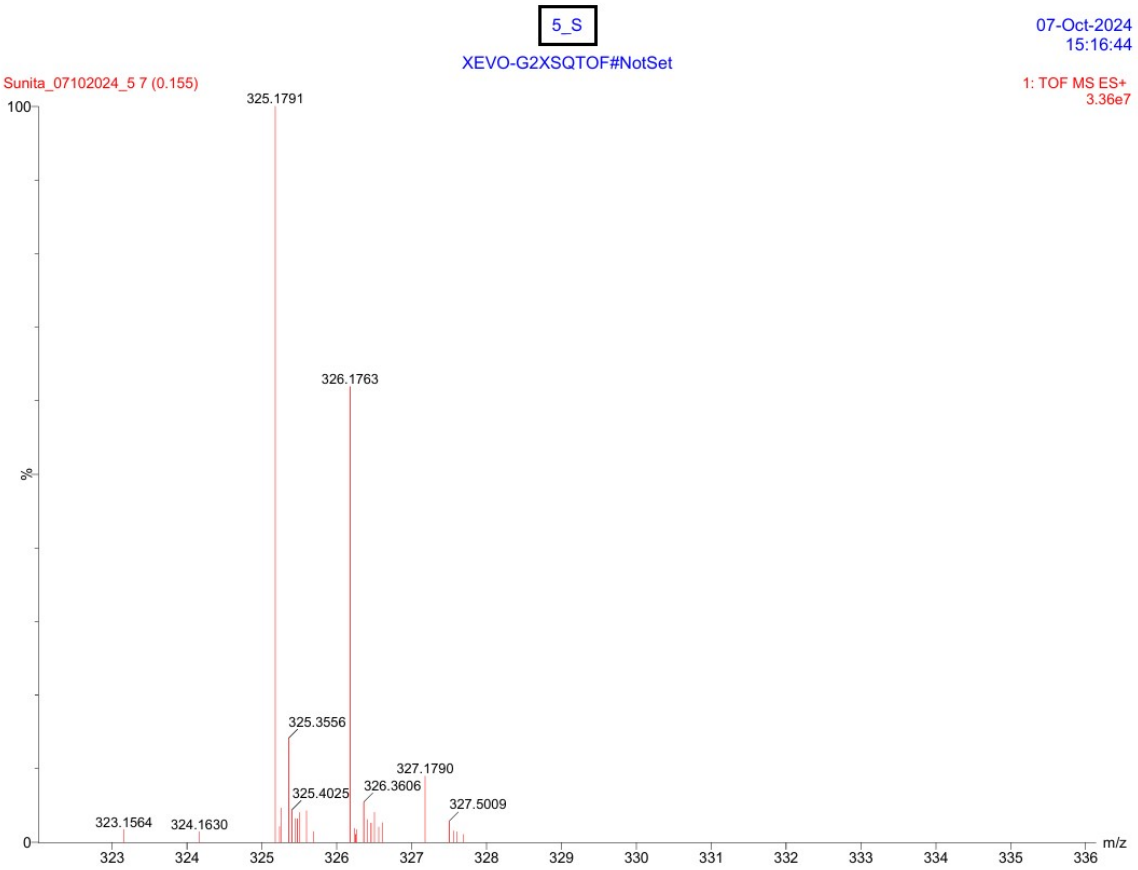


Figure S43: The HRMS profile of compound 5S.

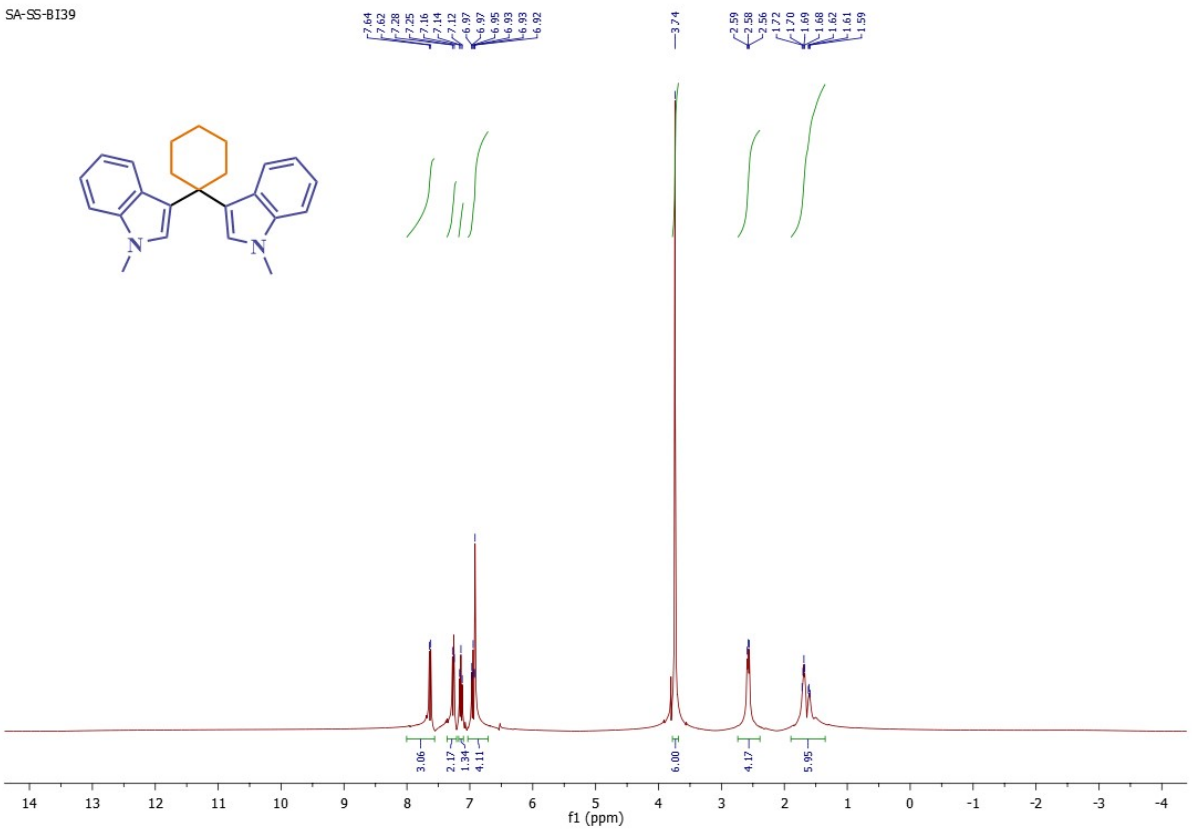


Figure S44: ^{1}H NMR spectrum of compound 5T.

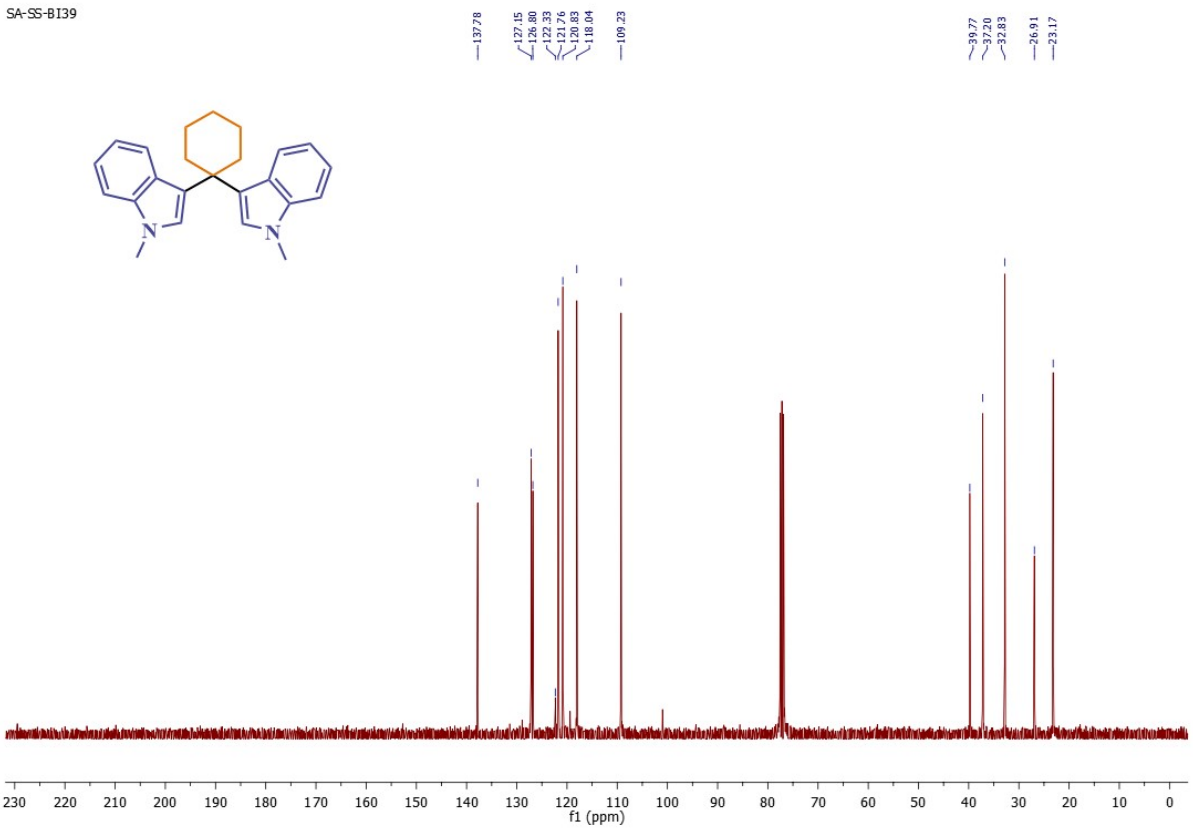


Figure S45: ^{13}C NMR spectrum of compound 5T.

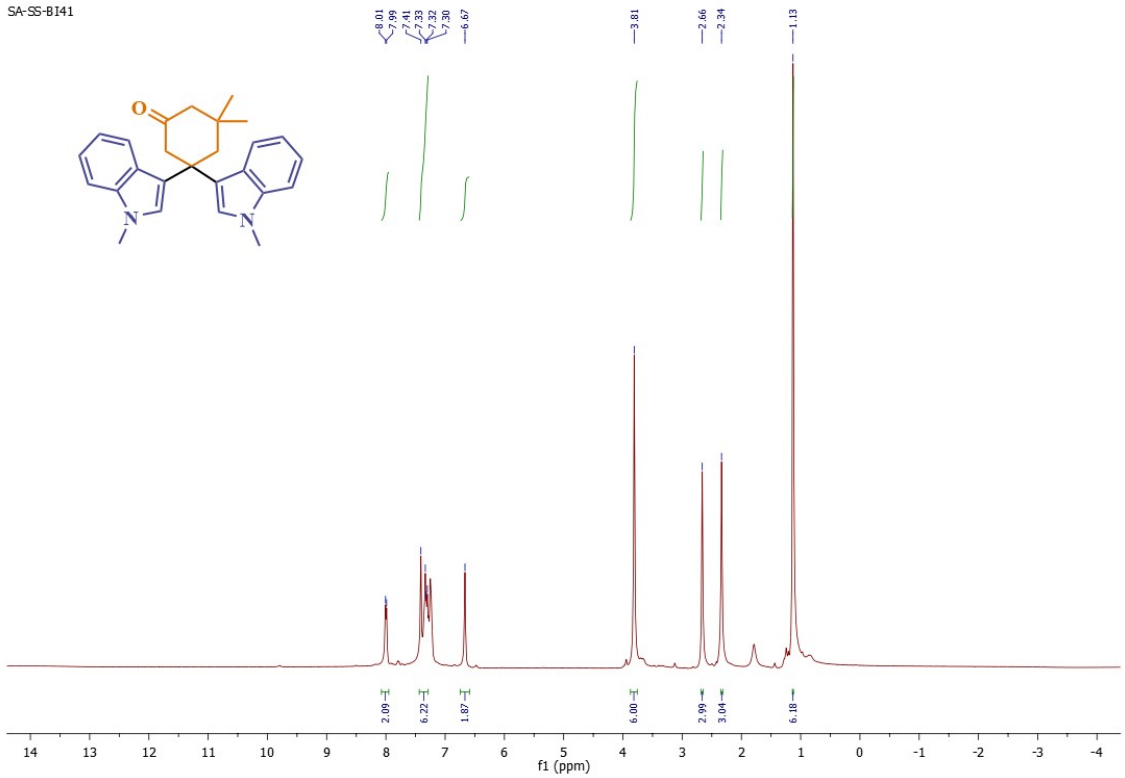


Figure S46: ^{1}H NMR spectrum of compound 5U.

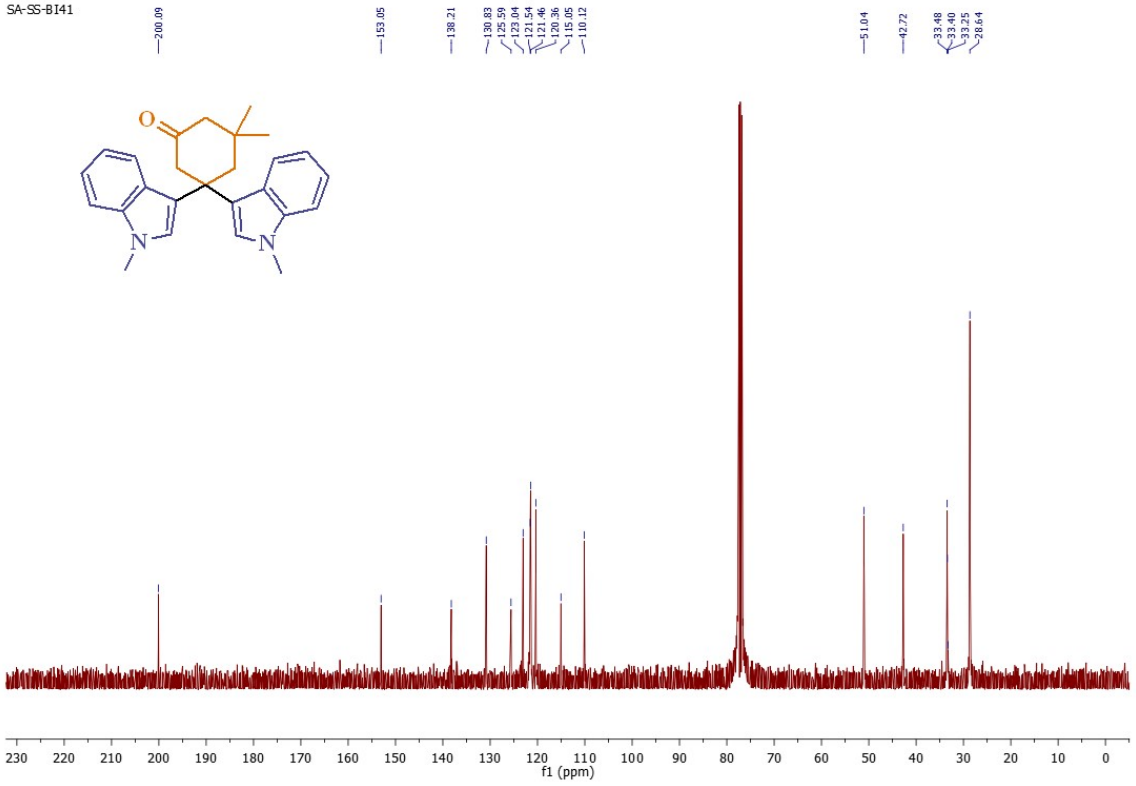


Figure S47: ^{13}C NMR spectrum of compound 5U.

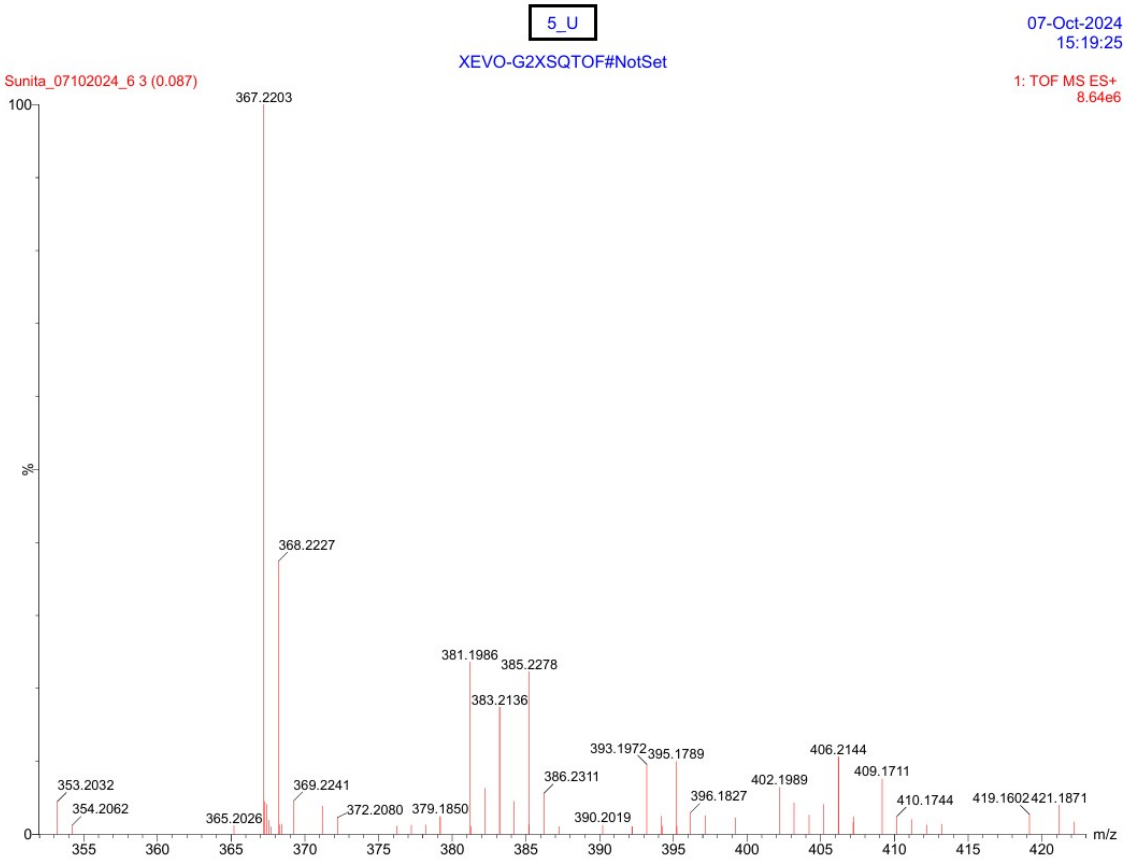


Figure S48: The HRMS profile of compound 5U.

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